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THE INSTITUTE OF THEORETICAL ASTROPHYSICS  
OSLO UNIVERSITY, NORWAY

SCIENTIFIC REPORT No. 14 (36) OF CONTRACT No. AF 61 (052) - 186

JØRGEN BERNHOFT KNOFF

THE BOLTZMANN EQUATION AND NON-EQUILIBRIUM  
PHENOMENA IN IONIZED GASES IN  
ELECTROMAGNETIC FIELDS

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**THE BOLTZMANN EQUATION AND NON-EQUILIBRIUM  
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## ABSTRACT

Boltzmann's equation, with a collision term differing somewhat from the usual and taking long-range interactions into account, is shown to be a correct basis for an analysis of physical phenomena in (ideal) ionized gases. All macroscopic quantities, including the electromagnetic field, are identified with statistical averages of the corresponding microscopic quantities.

We then consider the inherent tendency of the system towards statistical equilibrium, i.e. minimum or zero entropy production. A new proof is developed for the H-theorem, valid when the intermolecular forces are mainly of the long-range type. The characteristic times for the different relaxation processes are computed, and the equilibrium conditions for a rotating gas in external and internal force fields are deduced by exact methods.

The general theory of transport phenomena is then considered. The transport equations are derived, and it is shown that to get a complete set of equations it is necessary to postulate "phenomenological relations" between "fluxes" and "forces", these being defined in accordance with the conditions of equilibrium.

Making specific assumptions about the properties of symmetry of the gas when a magnetic field is present, we derive the proper form of the coefficient tensors with the aid of the theory of Cartesian tensors. The usual assumption that the tensors are isotropic is not justified.

Some important features of irreversible processes are discussed. We then proceed to solve Boltzmann's equation by successive approximations. The result thus obtained from microscopic theory are in complete accord with the results obtained earlier by macroscopic reasoning.

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## INTRODUCTION

The purpose of the present paper is to give a presentation of certain physical problems and mathematical methods encountered in that branch of physics which deals with ionized gases in electromagnetic fields.

Our aim is the description of non-equilibrium states of the system, that is phenomena of relaxation and transport. Considering the macroscopic behavior of the system to be identical with the averaged microscopic behavior, we shall build our theory on the most general microscopic basis. This is not, as almost invariably presupposed, the Boltzmann equation, but the more fundamental Liouville equation. From the latter equation one may, however, under certain conditions deduce the Boltzmann equation.

The microscopic description permits us to draw a number of interesting conclusions concerning the behavior of the ionized gas. In addition it permits an exact deduction of the macroscopic transport equations.

Special attention must be given to the inherent tendency of the system towards statistical equilibrium. While the intermolecular mechanism of interaction cannot be expected to have any influence upon the form of the final equilibrium conditions, it is essential for the rate of approach to this state. When computing the relaxation times of the system, full account must be taken of the long-range intermolecular forces. Such forces are predominant in ionized gases, a fact that has not always been given the deserved attention.

The form of the equilibrium conditions is essential to the definition of the "fluxes" and "forces" that are linearly connected in the phenomenological relations. As we shall see, the existence of these relations is necessary in order to get a complete set of equations. This is, consequently, in general only possible for states sufficiently near equilibrium. The form of the equilibrium conditions has most often been taken over from macroscopic, thermodynamical theory. Instead we shall deduce, from our microscopic equations, equilibrium conditions that are somewhat more general than the usual ones.

Many authors, when dealing with ionized gases, simply assume the validity of the usual macroscopic equations of classical fluid dynamics, and forget that an isotropic medium has been presupposed. It is, however, an important fact that a magnetic field will introduce an anisotropy in a medium composed of ionized molecules, giving it a rotational symmetry.

There are thus at least four frequent defects in earlier presentations of the theory of ionized gases, namely:

- a) The founding of the theories on Boltzmann's equation, which should be replaced by Liouville's equation.
- b) The failure to take into account the long-range intermolecular forces.
- c) The too special equilibrium conditions assumed.
- d) The failure to take into account the anisotropy of the medium introduced by a magnetic field.

These are considered to constitute a sufficient reason to give this presentation of the theory.

Our aim will then be to remove these defects and build up a consistent theory from a very general microscopic base.



## APPROXIMATIONS

The only approximations to be made from the outset are the following:

- a) No quantum-mechanical effects are considered.
- b) Relativistic effects are neglected, and the correlation region for the molecules are assumed to be sufficiently small so that the interactions inside this domain may be considered instantaneous.

Other approximations to be made in the course of development will be explicitly stated at the appropriate place in the text. They are in main:

- c) For the greater part the treatment will be restricted to "ideal gases", the mean kinetic energy being much greater than the electrostatic energy of interaction.
- d) The state of the system will usually be supposed to be near equilibrium. That is, the deviation in the macroscopic quantities from the equilibrium conditions of Section 16 are small. This validates a first-order theory.
- e) The effects of the surroundings of the system will usually be represented by external macroscopic force fields.

## NOTATION

Our notation mainly follows that of Chapman and Cowling [4]. The vector notation of Gibbs is adopted. Scalars, vectors and tensors of the second (and occasionally of higher) order are denoted by the following representative symbols:

$$s, \quad \mathbf{v}, \quad \mathbf{T}.$$

Simple scalar product is denoted by a dot, e.g.,  $\mathbf{u} \cdot \mathbf{v}$  or  $\mathbf{v} \cdot \mathbf{U}$ . Repeated scalar product is denoted by more than one dot, e.g.  $\mathbf{U} : \mathbf{V}$ . Instead of the usual symbol  $\nabla$ , the symbol  $\frac{\partial}{\partial \mathbf{r}}$  is adopted for the del or nabla operator, where  $\mathbf{r}$  is the position vector.

$\mathbf{I}$  is the unit (second order) tensor with components  $\delta_{ik}$  (Kronecker delta). The trace or divergence of a second order tensor  $\mathbf{U}$  is defined as

$$U_{ii} = \mathbf{U} : \mathbf{I} \quad (\text{summation over } i).$$

From any tensor  $\mathbf{U}$  a non-divergent tensor, denoted by  $\overset{\circ}{\mathbf{U}}$ , may be derived:

$$\overset{\circ}{\mathbf{U}} = \mathbf{U} - \frac{1}{3} U_{ii} \mathbf{I}.$$

If the elements of a tensor  $\mathbf{U}$  are  $U_{ik}$  a new tensor  $\tilde{\mathbf{U}}$ , the conjugate to  $\mathbf{U}$ , is defined having the elements  $\tilde{U}_{ik} = U_{ki}$ .

Any tensor  $\mathbf{U}$  may be written as the sum of a symmetrical and an antisymmetrical tensor:

$$\mathbf{U} = \frac{1}{2}(\mathbf{U} + \tilde{\mathbf{U}}) + \frac{1}{2}(\mathbf{U} - \tilde{\mathbf{U}}).$$

The other symbols used will be defined in the course of development.

## PART I. GENERAL THEORY

### 1. INTRODUCTORY REMARKS

When we undertake any given physical description, the *system* we wish to describe must be set off from the surrounding mass of all physical objects, i.e. the *environment*. In the following, our system is a certain quantity of gas, and the environment may consist of other gases, fluids or solid forms of matter. Fields of force will not be considered to be independent objects, but rather as being attributes of material systems, existing because of the internal structure of the latter or their motion.

A system may be divided into an arbitrary number of component systems, but the partition cannot, or need not, be indefinitely continued. We eventually arrive at a usually very large number of *elementary systems*, where we no longer need to know the internal structure of each system. We are only interested in the externally directed effect of the elementary system on its environment. From this point of view the interior of an elementary system does not belong to the proper system.

We thus define both an outer and an inner limit to our system. In our case the elementary systems are molecules, atoms and electrons, all of them possessing a certain electric charge and other molecular properties.

The *state* of the system is described by certain coordinates of state, the choice of which depends on the type of description we elect for our system. We are often content with a macroscopic description, and the coordinates then are quantities that refer to the system as a whole, i.e. pressure, temperature, volume, etc.

But more often than not such a description is too coarse, and we must apply a microscopic description. Here the macroscopic phenomena constitute nothing but the sum of a multitude of molecular effects.

The most detailed description possible of a system is made by giving the states of all the elementary systems. When the system is a gas, this means that we give the total number of molecular coordinates of state, such as position and velocity, for each molecule at a given time. Because of the large number of elementary systems in the proper system, we must usually resort to a statistical description.

If we are to describe the development of a system, we must know how the parts of the system interact with each other and with the environment. We must, in other words, know:

- a) The inwardly directed effects of the environment on the system (on the parts of the system, the elementary system).
- b) The outwardly directed effects of the elementary systems on their environments (i.e. the other elementary systems).

Concerning the latter effects we must postulate that the internal structure of the elementary systems is unchangeable and independent of the environment. If this is not the case, we must perform a further subdivision into new elementary systems. The externally directed effect of the elementary systems may then be represented by constant proper fields of force of different types, and can be considered as a molecular property. From a macroscopic point of view this will take the form of different types of fields

of force - electrical, gravitational, etc. Other forces are of the magnetic type, arising as a result of the electric transport of charge by the molecules.

We may expect that the environment can be divided into component and elementary fields, in the same way as for the proper system. From this point of view the effects a) of the environment on the system are the sums of all the separate effects of the elementary systems in the environment. These effects must be ascribed to the proper fields of the elementary systems and the forces arising from their motion.

The whole problem of interactions thus reduces to that of mutual effects between elementary systems. These we must know if we are to make an exact description of the development of a system. This really means that we extend the system so as to include part of the environment. The more exact we wish our description to be, the more we must extend the limits of our system, inwards and outwards.

By making certain assumptions, however, we can often describe the physical processes of a system without detailed knowledge of the environment. We may, for instance, assume that the system is sufficiently far removed from all environmental influences, so that interaction may be neglected. If this is not the case, we may assume that the effects can be represented by constant or time-dependent macroscopic fields of force, by various limiting conditions, and so on.

We now proceed to the treatment of gases, particularly ionized gases.

## 2. MICROSCOPIC AND STATISTICAL DESCRIPTION.

### BOLTZMANN'S EQUATION

Suppose that our system - a certain quantity of gas - consists of several component systems or gases, which we denote by the indices  $\alpha = 1, 2, \dots$ . Each component system is in turn composed of a large number of identical elementary systems or gas molecules. We assume that the internal structure of the elementary systems is constant, and that each molecule is surrounded by a constant proper field of forces. If the molecules have the electric charge  $e_\alpha$ , the potential of this force will be  $e_\alpha/r$ .

From a microscopic point of view, the state of the system is given when the position  $\mathbf{r}_{\alpha k}$  and the velocity  $\mathbf{c}_{\alpha k}$  of all molecules are given ( $k = 1, 2, \dots, v_\alpha$ , where  $v_\alpha$  is the total number of molecules of the type  $\alpha$ ). Each molecule may thus be represented by a point in a six-dimensional position-velocity space, the  $(\mathbf{r}, \mathbf{c})$ -space. The microscopic density of these points in  $(\mathbf{r}, \mathbf{c})$ -space is given by [1],

$$F_\alpha(\mathbf{r}, \mathbf{c}, t) = \sum_k \delta(\mathbf{r} - \mathbf{r}_{\alpha k}(t)) \delta(\mathbf{c} - \mathbf{c}_{\alpha k}(t)), \quad \alpha = 1, 2, \dots, \quad (1.1)$$

where  $\delta$  is Dirac's delta-function.

The microscopic density in position space is

$$N_\alpha(\mathbf{r}, t) = \int F_\alpha(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = \sum_k \delta(\mathbf{r} - \mathbf{r}_{\alpha k}(t)). \quad (1.2)$$

Now having defined the microscopic state of our system, we are interested in finding equations that describe the development of state with time.

The functions  $F_\alpha$  must satisfy the equation of continuity (Liouville's equation),

$$\frac{dF_\alpha}{dt} + \mathbf{c} \cdot \frac{dF_\alpha}{d\mathbf{r}} + \frac{d}{d\mathbf{c}} \cdot (F_\alpha \mathbf{F}_{\alpha m}) = 0, \quad (1.3)$$

where  $\mathbf{F}_{\alpha m}(\mathbf{r}, \mathbf{c}, t)$  is the total microscopic field of force. This is composed of the external field  $\mathbf{F}_{\alpha 0}$ , representing the effect of the environment on the system, and another force term which represents the effects of all the molecular fields of force on a particle  $\alpha$  in  $(\mathbf{r}, \mathbf{c})$ ,

$$\mathbf{F}_{\alpha m} = \mathbf{F}_{\alpha 0} + \sum_{\beta} \sum_k \mathbf{F}_{\alpha\beta}(\mathbf{r}, \mathbf{c}, \mathbf{r}_{\beta k}(t'), \mathbf{c}_{\beta k}(t')). \quad (1.4)$$

Here  $\mathbf{F}_{\alpha\beta}$  is the contribution to the field of force at the point  $(\mathbf{r}, \mathbf{c})$  from a particle  $\beta$  with the coordinates  $(\mathbf{r}_{\beta k}(t'), \mathbf{c}_{\beta k}(t'))$ . The latter term can also be written as

$$\begin{aligned} \sum_{\beta} \sum_k \int \mathbf{F}_{\alpha\beta}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}') \delta(\mathbf{r}' - \mathbf{r}_{\beta k}) \delta(\mathbf{c}' - \mathbf{c}_{\beta k}) d\mathbf{r}' d\mathbf{c}' = \\ = \sum_{\beta} \int \mathbf{F}_{\alpha\beta}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}') F_{\beta}(\mathbf{r}', \mathbf{c}', t') d\mathbf{r}' d\mathbf{c}'. \end{aligned} \quad (1.5)$$

The integration extends over all points  $\mathbf{r}'$  with the exception of the point  $\mathbf{r}' = \mathbf{r}$ , which must be excluded as we cannot include the contribution from the proper field of the particle  $\alpha$  in  $\mathbf{r}$ .

From this microscopic description we can now proceed to a statistical description. In so doing we regard all quantities as being functions of an initial configuration of particle coordinates  $(\mathbf{r}_{\alpha k}(0), \mathbf{c}_{\alpha k}(0), k = 1, 2, \dots, v_\alpha, \alpha = 1, 2, \dots)$ , and average over a certain set of such configurations. We denote the averaged quantities by  $\langle \rangle$ .

The mean quantity  $\langle F_\alpha \rangle$  is identical to the familiar distribution function

$$f_\alpha(\mathbf{r}, \mathbf{c}, t) = \langle F_\alpha \rangle = \langle F_\alpha(\mathbf{r}, \mathbf{c}, t) \rangle. \quad (1.6)$$

We may interpret  $f_\alpha d\mathbf{r} d\mathbf{c}$  as the probable number of particles  $\alpha$  in the element of volume  $d\mathbf{r} d\mathbf{c}$  in  $(\mathbf{r}, \mathbf{c})$ -space.

In a similar way we can define the distribution function of the second order,

$$\begin{aligned} f_{\alpha\beta}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}', t, t') &= \langle F_\alpha F_\beta' \rangle, & \alpha \neq \beta \\ f_{\alpha\alpha}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}', t, t') &= \langle F_\alpha F_\alpha' \rangle - \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{c} - \mathbf{c}') \langle F_\alpha \rangle, & \alpha = \beta \end{aligned} \quad (1.7)$$

Here  $f_{\alpha\beta} d\mathbf{r} d\mathbf{c} d\mathbf{r}' d\mathbf{c}'$  is proportional to the probability of finding a molecule  $\alpha$  in the element  $d\mathbf{r} d\mathbf{c}$  at the point  $(\mathbf{r}, \mathbf{c})$  simultaneously with the presence of a molecule of the type  $\beta$  in the element  $d\mathbf{r}' d\mathbf{c}'$  at the point  $(\mathbf{r}', \mathbf{c}')$  at the retarded time  $t' = t - \frac{|\mathbf{r} - \mathbf{r}'|}{c}$ . (We assume that all effects of force propagate at the velocity of light  $c$ .)

The definitions of the functions of higher order are closely analogous with expressions (1.6) and (1.7).

In the same way we can define statistical mean values of all quantities that depend on the particle coordinates  $\mathbf{r}_{\alpha k}$  and  $\mathbf{c}_{\alpha k}$ . If, for instance, we average the equation (1.3) we get

$$\frac{df_{\alpha}}{dt} + \mathbf{c} \cdot \frac{d\mathbf{f}_{\alpha}}{d\mathbf{r}} + \mathbf{F}_{\alpha 0} \cdot \frac{d\mathbf{f}_{\alpha}}{d\mathbf{c}} + \frac{d}{d\mathbf{c}} \cdot \sum_{\beta} \int \mathbf{F}_{\alpha\beta} f_{\alpha\beta} d\mathbf{r}' d\mathbf{c}' = 0. \quad (1.8)$$

In Section 8 we shall show that the last term of this equation partly gives origin to a correction to the external macroscopic field of force  $\mathbf{F}_{\alpha 0}$ , and partly to the so-called "collision term"  $\frac{d\mathbf{f}_{\alpha}}{dt}$ . Equation (1.8) may therefore be brought onto the form

$$\frac{df_{\alpha}}{dt} + \mathbf{c} \cdot \frac{d\mathbf{f}_{\alpha}}{d\mathbf{r}} + \mathbf{F}_{\alpha} \cdot \frac{d\mathbf{f}_{\alpha}}{d\mathbf{c}} = \frac{d\mathbf{f}_{\alpha}}{dt}, \quad \alpha = 1, 2, \dots \quad (1.9)$$

This is *Boltzmann's equation*, which is the fundamental point of departure of almost all exact treatments of the physical conditions in gases.

### 3. THE ELECTROMAGNETIC FIELD

The microscopic, electric and magnetic fields are composed of an external and an internal part,

$$\begin{aligned} \mathbf{E}_m(\mathbf{r}, t) &= \mathbf{E}_0(\mathbf{r}, t) + \sum_{\beta} \sum_k \mathbf{E}_{\beta}(\mathbf{r}, \mathbf{r}'_{\beta k}, \mathbf{c}'_{\beta k}), \\ \mathbf{B}_m(\mathbf{r}, t) &= \mathbf{B}_0(\mathbf{r}, t) + \sum_{\beta} \sum_k \mathbf{B}_{\beta}(\mathbf{r}, \mathbf{r}'_{\beta k}, \mathbf{c}'_{\beta k}). \end{aligned} \quad (1.10)$$

Here  $\mathbf{E}_{\beta}$  and  $\mathbf{B}_{\beta}$  are the contributions to the internal fields at a point  $\mathbf{r}$  from a molecule of the type  $\beta$  with position  $\mathbf{r}'_{\beta k}$  and velocity  $\mathbf{c}'_{\beta k}$ .

They may be derived from the scalar and vector potentials  $\phi_{\beta}$  and  $\mathbf{A}_{\beta}$  defined by

$$\begin{aligned} \phi_{\beta}(\mathbf{r}, t) &= \frac{e_{\beta}}{|\mathbf{r} - \mathbf{r}'_{\beta k}|} = \int \frac{e_{\beta} \delta(\mathbf{r}' - \mathbf{r}'_{\beta k}) \delta(\mathbf{c}' - \mathbf{c}'_{\beta k})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{c}', \\ \mathbf{A}_{\beta}(\mathbf{r}, t) &= \frac{1}{c} \frac{e_{\beta} \mathbf{c}_{\beta k}}{|\mathbf{r} - \mathbf{r}'_{\beta k}|} = \frac{1}{c} \int \frac{e_{\beta} \mathbf{c}' \delta(\mathbf{r}' - \mathbf{r}'_{\beta k}) \delta(\mathbf{c}' - \mathbf{c}'_{\beta k})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{c}'. \end{aligned} \quad (1.11)$$

We thus have the electric charge and current densities due to a molecule  $\beta$ :

$$\begin{aligned} \rho_e(\mathbf{r}, t) &= e_{\beta} \delta(\mathbf{r} - \mathbf{r}_{\beta k}) = \int e_{\beta} \delta(\mathbf{r} - \mathbf{r}_{\beta k}) \delta(\mathbf{c} - \mathbf{c}_{\beta k}) d\mathbf{c}, \\ \mathbf{j}_{e\beta}(\mathbf{r}, t) &= e_{\beta} \mathbf{c}_{\beta k} \delta(\mathbf{r} - \mathbf{r}_{\beta k}) = \int e_{\beta} \mathbf{c} \delta(\mathbf{r} - \mathbf{r}_{\beta k}) \delta(\mathbf{c} - \mathbf{c}_{\beta k}) d\mathbf{c}. \end{aligned} \quad (1.12)$$

It follows from the formulas (1.11) that the internal fields  $\mathbf{E}_{\beta}$  and  $\mathbf{B}_{\beta}$  defined by

$$\mathbf{E}_\beta = \frac{\partial}{\partial \mathbf{r}} \phi_\beta - \frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}_\beta ,$$

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{A}_\beta + \frac{1}{c} \frac{\partial}{\partial t} \phi_\beta = 0$$

$$\mathbf{B}_\beta = \frac{\partial}{\partial \mathbf{r}} \times \mathbf{A}_\beta , \quad (1.13)$$

satisfy a set of equations which is completely equivalent to Maxwell's equations for macroscopic fields (Brittin [2]),

$$\begin{aligned} \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{E}_\beta &= 4\pi q_{e\beta} , & \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{B}_\beta &= 0 \\ \frac{\partial}{\partial \mathbf{r}} \times \mathbf{E}_\beta &= -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{B}_\beta , & \frac{\partial}{\partial \mathbf{r}} \times \mathbf{B}_\beta &= \frac{1}{c} \frac{\partial}{\partial t} \mathbf{E}_\beta + \frac{4\pi}{c} \mathbf{j}_{e\beta} . \end{aligned} \quad (1.14)$$

The external fields  $\mathbf{E}_0$  and  $\mathbf{B}_0$ , which may be derived from the external potentials  $\phi_0$  and  $\mathbf{A}_0$ , naturally satisfy the corresponding homogeneous equations. It follows that the total microscopic fields (1.10) satisfy Maxwell's equations with the respective charge and current densities

$$q_{em} = \sum_\beta \sum_k q_{e\beta} = \sum_\beta \int e_\beta F_\beta (\mathbf{r}', \mathbf{c}', t') d\mathbf{r}' d\mathbf{c}' , \quad (1.15)$$

$$\mathbf{j}_{em} = \sum_\beta \sum_k \mathbf{j}_{e\beta} = \sum_\beta \int e_\beta \mathbf{c}' F_\beta (\mathbf{r}', \mathbf{c}', t') d\mathbf{r}' d\mathbf{c}' .$$

The fields  $\mathbf{E}_m$  and  $\mathbf{B}_m$  may then be derived from the total scalar and vector potentials

$$\phi_m = \phi_0 + \sum_\beta \sum_k \phi_\beta = \phi_0 + \sum_\beta \int \frac{e_\beta}{|\mathbf{r} - \mathbf{r}'|} F_\beta (\mathbf{r}', \mathbf{c}', t') d\mathbf{r}' d\mathbf{c}' , \quad (1.16)$$

$$\mathbf{A}_m = \mathbf{A}_0 + \sum_\beta \sum_k \mathbf{A}_\beta = \mathbf{A}_0 + \sum_\beta \int \frac{e_\beta \mathbf{c}'}{|\mathbf{r} - \mathbf{r}'|} F_\beta (\mathbf{r}', \mathbf{c}', t') d\mathbf{r}' d\mathbf{c}' .$$

Instead of the set (1.10) we can also write

$$\mathbf{E}_m = \mathbf{E}_0 + \sum_\beta \int \mathbf{E}_\beta (\mathbf{r}, \mathbf{r}', \mathbf{c}') F_\beta (\mathbf{r}', \mathbf{c}', t') d\mathbf{r}' d\mathbf{c}' , \quad (1.17)$$

$$\mathbf{B}_m = \mathbf{B}_0 + \sum_\beta \int \mathbf{B}_\beta (\mathbf{r}, \mathbf{r}', \mathbf{c}') F_\beta (\mathbf{r}', \mathbf{c}', t') d\mathbf{r}' d\mathbf{c}' .$$

The contribution to the force  $\mathbf{F}_{am}$  (1.4) from these fields is

$$\begin{aligned} \mathbf{F}_{\alpha m} &= \frac{e_{\alpha}}{m_{\alpha}} (\mathbf{E}_m + \frac{1}{c} \mathbf{c} \times \mathbf{B}_m) = \\ &= \frac{e_{\alpha}}{m_{\alpha}} \left[ (\mathbf{E}_0 + \frac{1}{c} \mathbf{c} \times \mathbf{B}_0) + \sum_{\beta} \int (\mathbf{E}_{\beta} + \frac{1}{c} \mathbf{c} \times \mathbf{B}_{\beta}) f'_{\beta} d\mathbf{r}' d\mathbf{c}' \right] . \end{aligned} \quad (1.18)$$

According to equations (1.17) the averaged macroscopic, electric and magnetic fields are

$$\mathbf{E} = \langle \mathbf{E}_m \rangle = \mathbf{E}_0 + \sum_{\beta} \int \mathbf{E}_{\beta} f'_{\beta} d\mathbf{r}' d\mathbf{c}' , \quad (1.19)$$

$$\mathbf{B} = \langle \mathbf{B}_m \rangle = \mathbf{B}_0 + \sum_{\beta} \int \mathbf{B}_{\beta} f'_{\beta} d\mathbf{r}' d\mathbf{c}' ,$$

while the averaged force  $\langle \mathbf{F}_{\alpha} \mathbf{F}_{\alpha m} \rangle$  which is included in equation (1.8) has the form

$$\langle \mathbf{F}_{\alpha} \mathbf{F}_{\alpha m} \rangle = \frac{e_{\alpha}}{m_{\alpha}} \left[ f_{\alpha} (\mathbf{E}_0 + \frac{1}{c} \mathbf{c} \times \mathbf{B}_0) + \sum_{\beta} \int (\mathbf{E}_{\beta} + \frac{1}{c} \mathbf{c} \times \mathbf{B}_{\beta}) f_{\alpha\beta} d\mathbf{r}' d\mathbf{c}' \right] . \quad (1.20)$$

Hence this force cannot be immediately expressed in the usual way by the fields  $\mathbf{E}$  and  $\mathbf{B}$ .

It follows from the above equations that the macroscopic fields  $\mathbf{E}$  and  $\mathbf{B}$  may be derived from the potentials  $\phi = \langle \phi_m \rangle$  and  $\mathbf{A} = \langle \mathbf{A}_m \rangle$ , and satisfy Maxwell's equations with charge density  $q_e = \langle q_{em} \rangle$  and  $\mathbf{j}_e = \langle \mathbf{j}_{em} \rangle$ .

#### 4. THE COLLISION TERM

The collision term  $\frac{d f_{\alpha}}{d t}$  represents the effects of direct interaction between molecules and their proper fields. The major difficulties in solving Boltzmann's equation are usually connected with this term.

We shall now discuss the conditions for a gas composed of two kinds of particles with positive and negative electric charge. We shall see in Section 4 that the correlation length for interaction between identical and non-identical particles  $D$  is given by

$$D = \left( \frac{\mathfrak{A}}{8 \pi e^2 n} \right)^{\frac{1}{2}} , \quad \mathfrak{A} = k T , \quad (1.21)$$

when  $e$ ,  $n$  and  $T$  is the electric charge, density and temperature, respectively, of the particles.

Two other distances of interest are

$$q_0 = \frac{e^2}{\mathfrak{A}} \quad \text{and} \quad d = n^{-\frac{1}{3}} . \quad (1.22)$$



Two particles that collide with each other with the impact parameter  $q_0$  will on the average be deflected by an angle  $\pi/2$ , and  $d$  is the mean distance between the particles.

If we now assume that the kinetic energy of the particles is much larger than the mean electrostatic energy of interaction, i.e.

$$\frac{e^2}{d} \ll \frac{1}{2} , \quad \frac{e^2}{\frac{1}{2}} = q_0 \ll d , \quad (1.23)$$

it follows immediately from expression (1.21) that

$$1 \ll nD^3 , \quad d \ll D . \quad (1.24)$$

The assumption (1.23) is nearly always satisfied. The impact parameter  $q_0$  for deflection at a right angle is thus much smaller than the mean particle distance, and the latter is much smaller than the correlation distance  $D$ ,

$$q_0 \ll d \ll D . \quad (1.25)$$

Employing the usual terminology [3], we let the term "short-range collisions" mean interactions between particles with impact parameter in the region  $(0, q_0)$ . As  $q_0 \ll d$ , such collisions will practically always be binary. The contribution of these interactions to the collision term  $\frac{d f_\alpha}{dt}$  is given by the binary collision integral [4],

$$\frac{d f_\alpha}{dt} = \sum_\beta \left( \frac{d f_\alpha}{dt} \right)_\beta = \sum_\beta \int [f_\alpha(c'_\alpha) f_\beta(c'_\beta) - f_\alpha(c_\alpha) f_\beta(c_\beta)] w_{\alpha\beta} b db d\epsilon d c_\beta , \quad (1.26)$$

where  $w_{\alpha\beta} = |(\mathbf{c}_\alpha - \mathbf{c}_\beta)|$  is the relative velocity between two particles  $\alpha$  and  $\beta$  before collision. The quantities  $\mathbf{c}_\alpha$  and  $\mathbf{c}_\beta$  are the velocities of the particles after collision, and are functions of  $\mathbf{c}_\alpha$ ,  $\mathbf{c}_\beta$  and  $b$ . The impact parameter  $b$  - the distance of closest approach of the particles in the absence of mutual influences - and the polar angle  $\epsilon$  characterize the collision geometrically. The region of integration of  $b$  is  $(0, q_0)$ .

When the impact parameter  $b$  lies in the region  $(q_0, d)$  we no longer may assume the collisions to be binary. Encounters with more than two participating particles will be equally probable.

Interactions with impact parameter in the region  $(d, D)$  may no longer be characterized as collisions. The change in the state of motion of a particle arises from a simultaneous interaction with a very great number of particles. In view of the large number of particles, the sum of the many weak effects of this kind most often becomes much larger than the relatively few, but strong binary collisions (Section 13). Such multiple interactions are called "long-range interactions".

We shall see in Section 10 that such multiple interactions can be represented by a "collision integral" of the Fokker-Planck type, first derived by Landau [5],

$$\begin{aligned} \frac{d f_{\alpha}}{d t} &= \sum_{\beta} \left( \frac{d f_{\alpha}}{d t} \right)_{\beta} = \\ &= - \sum_{\beta} \frac{2 \pi \lambda e_{\alpha}^2 e_{\beta}^2}{m_{\alpha}} \frac{d}{d \mathbf{c}} \cdot \int \mathbf{U} \cdot \left( \frac{f_{\alpha}}{m_{\beta}} \frac{d f_{\beta}}{d \mathbf{c}'} - \frac{f_{\beta}}{m_{\alpha}} \frac{d f_{\alpha}}{d \mathbf{c}} \right) d \mathbf{c}' . \end{aligned} \quad (1.27)$$

Here  $\lambda = \ln(D/q_0)$  is a cut-off factor which arises from the fact that we have taken into consideration interactions with impact parameter in the region  $(q_0, D)$ . We have thus included the contribution from the transition zone  $(q_0, d)$ . The quantities  $e_{\alpha}$  and  $e_{\beta}$  are the respective charges of the particles  $\alpha$  and  $\beta$ , while  $m_{\alpha}$  and  $m_{\beta}$  are their corresponding masses. Further,  $f_{\alpha} = f_{\alpha}(\mathbf{c})$  and  $f_{\beta} = f_{\beta}(\mathbf{c}')$  are the distribution functions for the two types of particles. The tensor  $\mathbf{U}$  is defined as

$$\mathbf{U} = \frac{1}{u^3} (u^2 \mathbf{I} - \mathbf{u} \mathbf{u}), \quad \mathbf{u} = \mathbf{c} - \mathbf{c}', \quad u = |\mathbf{u}|, \quad (1.28)$$

where  $\mathbf{I}$  is the unit tensor.

Interactions between particles with impact parameter larger than the distance  $D$  may be characterized as plasma oscillations [6]. Their effect must be included in the macroscopic force term in Boltzmann's equation.

Before turning to the exact derivation of Boltzmann's equation and the determination of the collision term (1.27), we shall take a look at the connection between the macroscopic and the (statistical) microscopic quantities of a gas.

## 5. MACROSCOPIC AND MICROSCOPIC QUANTITIES

The distribution function  $f_{\alpha} = f_{\alpha}(\mathbf{r}, \mathbf{c}, t)$  gives the density of an aggregation of identical molecules  $\alpha$  at the point  $(\mathbf{r}, \mathbf{c})$  in phase space at the time  $t$ . By definition, the distribution function can only have a statistical interpretation. The macroscopic, measurable quantities in which we are interested may be identified as mean values over velocity space of microscopic quantities with the weight factor  $f_{\alpha}$ . If, therefore, we can find in what way  $f_{\alpha}$  depends on  $\mathbf{r}$ ,  $\mathbf{c}$  and  $t$ , we have the exact solution to the relevant physical problem. The microscopic quantities mentioned are always various kinds of molecular properties, such as number, momentum, energy, mass and electric charge. We let  $\phi = \phi(\mathbf{r}, \mathbf{c}, t)$  denote the molecular property (generally a function of the position  $\mathbf{r}$  and velocity  $\mathbf{c}$  of the molecule, as well as the time  $t$ ), and define the mean value of  $\phi$  for the molecules  $\alpha$  in the following manner,

$$n_{\alpha} \bar{\phi}_{\alpha} = \int \phi_{\alpha} f_{\alpha} d\mathbf{c}_{\alpha}, \quad n_{\alpha} = \int f_{\alpha} d\mathbf{c}_{\alpha}. \quad (1.29)$$

Here  $n_{\alpha}$  is the density of the molecules  $\alpha$  in coordinate space. In general, both  $n_{\alpha}$  and  $\bar{\phi}_{\alpha}$  are functions of  $\mathbf{r}$  and  $t$ , while  $\phi$  may be a scalar, a vector or a tensor.

If the gas is made up of several component gases ( $\alpha = 1, 2, \dots$ ), we define the mean value  $\bar{\phi} = \bar{\phi}(\mathbf{r}, t)$  for the whole gas by the expression

$$n \bar{\phi} = \sum_{\alpha} n_{\alpha} \bar{\phi}_{\alpha} = \sum_{\alpha} \int \phi_{\alpha} f_{\alpha} d\mathbf{e}_{\alpha} , \quad (1.30)$$

where  $n = \sum_{\alpha} n_{\alpha}$  is the total gas density.

For the mean velocity, for instance, we get

$$n \bar{\mathbf{e}} = \sum_{\alpha} n_{\alpha} \bar{\mathbf{e}}_{\alpha} = \sum_{\alpha} \int \mathbf{e}_{\alpha} f_{\alpha} d\mathbf{e}_{\alpha} , \quad (1.31)$$

instead of which, however, general usage prefers the mass velocity  $\mathbf{e}_0$ ,

$$q \mathbf{e}_0 = n \overline{m \mathbf{e}} = \sum_{\alpha} n_{\alpha} \overline{m_{\alpha} \mathbf{e}_{\alpha}} = \sum_{\alpha} q_{\alpha} \bar{\mathbf{e}}_{\alpha} = \sum_{\alpha} q_{\alpha} \mathbf{e}_{\alpha 0} , \quad (1.32)$$

where each molecule is given a weight which is proportional to the mass of the molecule  $m_{\alpha}$ . The quantity  $q_{\alpha} = n_{\alpha} m_{\alpha}$  is the partial mass density, and  $q = \sum_{\alpha} q_{\alpha}$  is the total mass density. The momentum of the gas per

unit volume is evaluated as if each molecule moved with the velocity  $\mathbf{e}_{\alpha 0}$ . The mass velocity  $\mathbf{e}_{\alpha 0}$  of a component gas coincides with the mean velocity  $\bar{\mathbf{e}}_{\alpha}$ .

The thermal velocity  $\mathbf{C}_{\alpha}$  of a molecule in a composite gas is generally defined in relation to the mass velocity,

$$\mathbf{C}_{\alpha} = \mathbf{e}_{\alpha} - \mathbf{e}_0 , \quad \text{i.e.} \quad \sum_{\alpha} q_{\alpha} \bar{\mathbf{C}}_{\alpha} = \mathbf{0} . \quad (1.33)$$

The components of this vector are denoted by (U, V, W).

If we treat each component gas as a simple, independent gas, it is more natural to define the thermal velocity as

$$\mathbf{C}'_{\alpha} = \mathbf{e}_{\alpha} - \mathbf{e}_{\alpha 0} , \quad \text{i.e.} \quad \bar{\mathbf{C}}'_{\alpha} = \mathbf{0} . \quad (1.34)$$

In the following we shall, in general, use the first definition, but we shall also have occasion to make use of the latter viewpoint.

The mean thermal energy of the gas ( $\phi = \frac{1}{2} m C^2$ ) is

$$n \overline{\left( \frac{1}{2} m C^2 \right)} = \sum_{\alpha} n_{\alpha} \overline{\left( \frac{1}{2} m_{\alpha} C_{\alpha}^2 \right)} = \frac{3}{2} n k T , \quad \text{where } k = kT . \quad (1.35)$$

This is to be considered as a *definition* of the temperature T.

## 6. FLOW OF MOLECULAR PROPERTIES

We shall now investigate the flow of molecules through a small "test surface" with area  $dS$  and positive normal direction  $\mathbf{n}$  [4]. The velocity of the surface element is  $\mathbf{e}_f$ . The relative velocity of a molecule with respect to  $dS$  is

$$\mathbf{C}_{\alpha}^{rel} = \mathbf{e}_{\alpha} - \mathbf{e}_f = \mathbf{e}_0 + \mathbf{C}_{\alpha} - \mathbf{e}_f . \quad (1.36)$$

We consider molecules with thermal velocity  $\mathbf{C}_\alpha$  in the interval  $d\mathbf{C}_\alpha$ . In the course of a short time all the molecules in the group that were originally contained in the volume

$$d\mathbf{r} = \mathbf{C}_\alpha^{rel} \cdot dt d\mathbf{S} = \mathbf{n} \cdot \mathbf{C}_\alpha^{rel} dt d\mathbf{S}$$

will pass through  $d\mathbf{S}$ . The number of molecules thus is

$$f_\alpha d\mathbf{C}_\alpha (\mathbf{n} \cdot \mathbf{C}_\alpha^{rel}) dt d\mathbf{S} . \quad (1.37)$$

If each molecule carries along the molecular property  $\phi_\alpha(\mathbf{C}_\alpha)$ , the total amount of this property passing through the surface  $d\mathbf{S}$  during the interval of time  $dt$  will equal

$$\mathbf{n} \cdot \mathbf{C}_\alpha^{rel} \phi_\alpha f_\alpha d\mathbf{C}_\alpha dt d\mathbf{S} . \quad (1.38)$$

The total amount due to all molecules  $\alpha$  per unit time and unit area then becomes

$$\int \mathbf{n} \cdot \mathbf{C}_\alpha^{rel} \phi_\alpha f_\alpha d\mathbf{C}_\alpha = n_\alpha (\overline{\phi_\alpha \mathbf{C}_\alpha^{rel}}) . \quad (1.39)$$

This is the component along  $\mathbf{n}$  of the vector (or tensor)  $n_\alpha (\overline{\phi_\alpha \mathbf{C}_\alpha^{rel}})$ , which further equals

$$n_\alpha (\overline{\phi_\alpha \mathbf{C}_\alpha^{rel}}) = n_\alpha (\overline{\phi_\alpha \mathbf{C}_\alpha}) + n_\alpha (\mathbf{c}_0 - \mathbf{c}_f) \bar{\phi}_\alpha . \quad (1.40)$$

The last, so-called convective part, disappears when the test surface  $d\mathbf{S}$  moves with the mean velocity of the molecules  $\mathbf{c}_0$ . In this case we obtain for the flux of the property  $\phi$ ,

$$n_\alpha (\overline{\phi_\alpha \mathbf{C}_\alpha}) , \quad (1.41)$$

which we call the "flux vector" of the property  $\phi$ .

The flux vector for the number of particles ( $\phi_\alpha = 1$ ) thus is

$$n_\alpha \bar{\mathbf{C}}_\alpha , \quad (1.42)$$

and disappears for a simple gas. It is also called the "diffusion vector" of the molecules  $\alpha$ .

The flux vector of momentum is found by putting  $\phi = m\mathbf{C}$ , which gives

$$n (\overline{m_\alpha \mathbf{C}_\alpha \mathbf{C}_\alpha}) = \mathbf{P}_\alpha . \quad (1.43)$$

Another term for this tensor is the "stress tensor" of the molecules  $\alpha$ .

In the same way the flux vector of energy ( $\phi = \frac{1}{2} m\mathbf{C}^2$ ) is

$$n_\alpha (\overline{\frac{1}{2} m_\alpha \mathbf{C}_\alpha^2 \mathbf{C}_\alpha}) = \mathbf{q}_\alpha . \quad (1.44)$$

This vector is usually called the "heat flow" of the molecules  $\alpha$ .

The expressions

$$n_{\alpha} \bar{\mathbf{C}}_{\alpha} , \quad \mathbf{P} \quad \text{and} \quad \mathbf{q}_{\alpha}$$

thus give the flux of the number of particles, momentum and thermal energy through a surface which follows the mean motion of the gas. The flux of a molecular property which is independent of the velocity,  $\phi_{\alpha} = K_{\alpha}$ , (e.g. mass and electric charge) is evidently given by the vector

$$n_{\alpha} K_{\alpha} \bar{\mathbf{C}}_{\alpha} . \quad (1.45)$$

The total contribution for all component gases  $\alpha$  is of course the sum of the single contributions,

$$\begin{aligned} n \bar{\mathbf{K}} \bar{\mathbf{C}} &= \sum_{\alpha} n_{\alpha} K_{\alpha} \bar{\mathbf{C}}_{\alpha} , \\ \mathbf{P} &= nm \bar{\mathbf{C}} \bar{\mathbf{C}} = \sum_{\alpha} n_{\alpha} m_{\alpha} \bar{\mathbf{C}}_{\alpha} \bar{\mathbf{C}}_{\alpha} = \sum_{\alpha} \mathbf{P}_{\alpha} , \\ \mathbf{q} &= n \frac{1}{2} m \bar{\mathbf{C}}^2 \bar{\mathbf{C}} = \sum_{\alpha} \frac{1}{2} n_{\alpha} m_{\alpha} \bar{\mathbf{C}}_{\alpha}^2 \bar{\mathbf{C}}_{\alpha} = \sum_{\alpha} \mathbf{q}_{\alpha} . \end{aligned} \quad (1.46)$$

According to equation (1.33) the mass flux vector ( $K_{\alpha} = m_{\alpha}$ ) becomes zero, while the electric charge flux vector ( $K_{\alpha} = e_{\alpha}$ ) becomes

$$\mathbf{j}^* = n e \bar{\mathbf{C}} = \sum_{\alpha} n_{\alpha} e_{\alpha} \bar{\mathbf{C}}_{\alpha} = \sum_{\alpha} n_{\alpha} e_{\alpha} \bar{\mathbf{e}}_{\alpha} - \left( \sum_{\alpha} n_{\alpha} e_{\alpha} \right) \mathbf{e}_0 . \quad (1.47)$$

This, therefore, is identical to the conductive current density, which is the difference between the total current density and the convective flow.

The flux of momentum, or the force transported in the gas through a surface with the normal direction  $\mathbf{e}_i$  is

$$\mathbf{P}_i = \mathbf{e}_i \cdot \mathbf{P} = \mathbf{P} \cdot \mathbf{e}_i = nm \bar{C}_i \bar{\mathbf{C}} , \quad (1.48)$$

$\mathbf{P}$  being symmetrical. Part of this force,

$$P_{ii} = \mathbf{e}_i \cdot \mathbf{P} \cdot \mathbf{e}_i = n(m \bar{C}_i^2) \quad (\text{no summation}) , \quad (1.49)$$

works perpendicularly to the surface, and is a pure pressure force, while the remainder works parallel to the surface, and is a pure shear force.

For instance,

$$P_{ik} = \mathbf{e}_i \cdot \mathbf{P} \cdot \mathbf{e}_k = n(m \bar{C}_i \bar{C}_k) , \quad k \neq i , \quad (1.50)$$

is the force working in the direction  $\mathbf{e}_k$  on a surface with the normal  $\mathbf{e}_i$ .

Writing the stress tensor on matrix form,

$$[\mathbf{p}] = [q \bar{\mathbf{C}} \bar{\mathbf{C}}] = q \begin{bmatrix} \overline{U^2} & \overline{UV} & \overline{UW} \\ \overline{VU} & \overline{V^2} & \overline{VW} \\ \overline{WU} & \overline{WV} & \overline{W^2} \end{bmatrix} = \begin{bmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{bmatrix}, \quad (1.51)$$

we see that the diagonal terms represent the pressure forces, while the other terms represent the shear forces.

The hydrostatic pressure is defined as the divergence of  $\mathbf{p}$ ,

$$\begin{aligned} p &= \frac{1}{3} (p_{xx} + p_{yy} + p_{zz}) = \frac{1}{3} p_{ii} = \frac{1}{3} \mathbf{p} : \mathbf{I} = \\ &= \frac{1}{3} nm (\bar{U}^2 + \bar{V}^2 + \bar{W}^2) = \frac{1}{3} q \bar{C}^2. \end{aligned} \quad (1.52)$$

In the case of equipartition of energy, with a contribution  $\frac{1}{2}kT$  for each degree of freedom, we get

$$p = nkT = n \frac{1}{2} kT. \quad (1.53)$$

The tensor  $\mathbf{p}$  can be split into two parts ( $\mathbf{I}$  = unit tensor),

$$\mathbf{p} = \overset{0}{\mathbf{p}} + \frac{1}{3} (\mathbf{p} : \mathbf{I}) \mathbf{I}. \quad (1.54)$$

The first, divergence-free part is the *shear-stress tensor*, and the other part, the *pressure tensor*, represents the scalar pressure.

Analogously with equation (1.51) we can write the heat flow as a column matrix,

$$[\mathbf{q}] = \left[ n \frac{1}{2} m C^2 \bar{\mathbf{C}} \right] = \frac{1}{2} q \begin{bmatrix} \overline{C^2 U} \\ \overline{C^2 V} \\ \overline{C^2 W} \end{bmatrix} = \begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix}, \quad (1.55)$$

where the terms represent the energy flux in the three coordinate directions. We may use a similar denotation for all vectors, e.g. the diffusion vector.

The tensor  $\mathbf{p}$  and other tensors may of course also be represented by column matrices, where the nine terms follow each other in a predetermined way. We shall use this form of expression on a later occasion (Section 21).

## 7. THE MACROSCOPIC TRANSPORT EQUATIONS

If we perform a transformation of coordinates from the set  $(\mathbf{r}, \mathbf{c}_\alpha, t)$  to the set  $(\mathbf{r}, \mathbf{C}_\alpha, t)$ ,  $\mathbf{C}_\alpha = \mathbf{c}_\alpha - \mathbf{c}_0$ , then Boltzmann's equation assumes the form

$$\frac{df_\alpha}{dt} + \mathbf{C}_\alpha \cdot \frac{\partial f_\alpha}{\partial \mathbf{r}} + (\mathbf{F}_\alpha - \frac{d\mathbf{c}_0}{dt}) \cdot \frac{\partial f_\alpha}{\partial \mathbf{C}_\alpha} - \frac{\partial f_\alpha}{\partial \mathbf{C}_\alpha} \mathbf{C}_\alpha : \frac{\partial}{\partial \mathbf{r}} \mathbf{c}_0 = \frac{\partial_c f_\alpha}{\partial t}, \quad (1.56)$$

where

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{c}_0 \cdot \frac{\partial}{\partial \mathbf{r}}.$$

(Two points: between dyadics means that scalar multiplication is twice repeated.)

If we multiply this equation by  $\phi_\alpha d\mathbf{C}_\alpha$  where  $\phi_\alpha(\mathbf{r}, \mathbf{C}_\alpha, t)$  is a molecular property, and next integrate over velocity space, we obtain an equation to determine the course of development of the corresponding macroscopic quantity  $n_\alpha \bar{\phi}_\alpha$ ,

$$\begin{aligned} \frac{dn_\alpha \bar{\phi}_\alpha}{dt} + n_\alpha \bar{\phi}_\alpha \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{c}_0 + \frac{\partial}{\partial \mathbf{r}} \cdot (n_\alpha \overline{\mathbf{C}_\alpha \phi_\alpha}) - n_\alpha \left[ \overline{\frac{d\phi_\alpha}{dt}} + \overline{\mathbf{C}_\alpha \cdot \frac{\partial \phi_\alpha}{\partial \mathbf{r}}} + \right. \\ \left. + (\mathbf{F}_\alpha - \frac{d\mathbf{c}_0}{dt}) \cdot \overline{\frac{\partial \phi_\alpha}{\partial \mathbf{C}_\alpha}} + (\frac{\partial}{\partial \mathbf{C}_\alpha} \cdot \mathbf{F}_\alpha) \bar{\phi}_\alpha - \overline{\frac{\partial \phi_\alpha}{\partial \mathbf{C}_\alpha} \mathbf{C}_\alpha : \frac{\partial}{\partial \mathbf{r}} \mathbf{c}_0} \right] = n_\alpha \frac{\partial_c \bar{\phi}_\alpha}{\partial t}. \end{aligned} \quad (1.57)$$

The right-hand side is defined by

$$n_\alpha \frac{\partial_c \bar{\phi}_\alpha}{\partial t} = \int \phi_\alpha \frac{\partial_c f_\alpha}{\partial t} d\mathbf{C}_\alpha, \quad (1.58)$$

and gives the time change of the total amount of properties  $\phi_\alpha$  in unit volume due to the collisions experienced by the molecular carriers  $\alpha$  of the property.

The other effects contributing to the total time change of the property  $\phi_\alpha$  in unit volume are:

- The net flux of molecules out of or into the volume.
- The way in which  $\phi_\alpha$  depends on position and velocity, and on time.

If we substitute  $\mathbf{C}'_\alpha$  for  $\mathbf{C}_\alpha$  from equation (1.34), then Boltzmann's equation (1.56) and the macroscopic equation (1.57) will have precisely the same form, provided that we replace  $\mathbf{C}_\alpha$  by  $\mathbf{C}'_\alpha$ , and  $\mathbf{c}_0$  by  $\mathbf{C}_{\alpha 0}$  everywhere.

We can now insert a set of microscopic quantities in equation (1.57), obtaining a corresponding set of macroscopic transport equations. The three transport equations for the number of particles ( $\phi = 1$ ), momentum ( $\phi = m\mathbf{C}$ ) and energy ( $\phi = \frac{1}{2}mC^2$ ) are of special interest. We shall return to these equations later.

We now proceed to the exact derivation of Boltzmann's equation (1.9) and the determination of the collision term (1.27).

## 8. DERIVATION OF BOLTZMANN'S EQUATION

The averaged Liouville's equation (1.8) has the form

$$\frac{\partial f_a}{\partial t} + \mathbf{c} \cdot \frac{\partial f_a}{\partial \mathbf{r}} + \mathbf{F}_{a0} \cdot \frac{\partial f_a}{\partial \mathbf{c}} + \frac{\partial}{\partial \mathbf{c}} \cdot \sum_{\beta} \int \mathbf{F}_{a\beta} f_{a\beta} d\mathbf{r}' d\mathbf{c}' = 0. \quad (1.59)$$

No approximations have been made so far. In the case of only electric and magnetic fields, we have, according to (1.20)

$$\mathbf{F}_{a0} = \frac{q_a}{m_a} (\mathbf{E}_0 + \frac{1}{c} \mathbf{c} \times \mathbf{B}_0), \quad \mathbf{F}_{a\beta} = \frac{e_a}{m_a} (\mathbf{E}_{\beta} + \frac{1}{c} \mathbf{c} \times \mathbf{B}_{\beta}),$$

As a result of interactions, the particles will not move independent of each other, certain *correlations* will exist between the motions of the individual particles. This physical condition may be mathematically formulated by letting  $f_{a\beta}$  have the form,

$$f_{a\beta}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}', t, t') = f_a(\mathbf{r}, \mathbf{c}, t) f_{\beta}(\mathbf{r}', \mathbf{c}', t') + \varphi_{a\beta}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}', t, t'). \quad (1.60)$$

The correlation factor  $\varphi_{a\beta}$  is only important in a region, the dimensions of which is the correlation length ( $|\mathbf{r} - \mathbf{r}'| \lesssim D$ ).

The distribution functions of higher orders have corresponding forms. We can for instance write  $f_{a\beta\gamma}$ :

$$\begin{aligned} f_{a\beta\gamma}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}', \mathbf{r}'', \mathbf{c}'', t, t', t'') = & f_a(\mathbf{r}, \mathbf{c}, t) f_{\beta}(\mathbf{r}', \mathbf{c}', t') f_{\gamma}(\mathbf{r}'', \mathbf{c}'', t'') + \\ & + f_a(\mathbf{r}, \mathbf{c}, t) \varphi_{\beta\gamma}(\mathbf{r}', \mathbf{c}', \mathbf{r}'', \mathbf{c}'', t', t'') + f_{\beta}(\mathbf{r}', \mathbf{c}', t') \varphi_{\gamma a}(\mathbf{r}'', \mathbf{c}'', \mathbf{r}, \mathbf{c}, t, t') + \\ & + f_{\gamma}(\mathbf{r}'', \mathbf{c}'', t'') \varphi_{a\beta}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}', t, t') + \varphi_{a\beta\gamma}(\mathbf{r}, \mathbf{c}, \mathbf{r}', \mathbf{c}', \mathbf{r}'', \mathbf{c}'', t, t', t''). \end{aligned} \quad (1.61)$$

When equation (1.60) is substituted, equation (1.59) assumes the form

$$\frac{\partial f_a}{\partial t} + \mathbf{c} \cdot \frac{\partial f_a}{\partial \mathbf{r}} + \mathbf{F}_a \cdot \frac{\partial f_a}{\partial \mathbf{c}} + \frac{\partial}{\partial \mathbf{c}} \cdot \sum_{\beta} \int \mathbf{F}_{a\beta} \varphi_{a\beta} d\mathbf{r}' d\mathbf{c}' = 0, \quad (1.62)$$

The total macroscopic field of force  $\mathbf{F}$  is expressed in the usual manner by the averaged electric and magnetic fields  $\mathbf{E} = \langle \mathbf{E}_m \rangle$  and  $\mathbf{B} = \langle \mathbf{B}_m \rangle$  defined by equation (1.19) (plus forces of different origin).

We permit ourselves to assume that the correlation region where  $\varphi_{a\beta}$  differs from zero is so small that no noticable error is committed by neglecting the time retardation and other relativistic effects within this area. We may then neglect the magnetic interaction between the particles, and only take account of the electrostatic interaction. Equation (1.62) then reduces to

$$\frac{\partial f_a}{\partial t} + \mathbf{c} \cdot \frac{\partial f_a}{\partial \mathbf{r}} + \mathbf{F}_a \cdot \frac{\partial f_a}{\partial \mathbf{c}} + \frac{\partial}{\partial \mathbf{c}} \cdot \sum_{\beta} \frac{e_a e_{\beta}}{m_a} \int \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \varphi_{a\beta} d\mathbf{r}' d\mathbf{c}' = 0, \quad (1.63)$$



where

$$\mathbf{F}_\alpha = \frac{e_\alpha}{m_\alpha} (\mathbf{E} + \frac{1}{c} \mathbf{c} \times \mathbf{B}) .$$

Equation (1.63) is the starting point of at least two important recent investigations, the first by Kadomtsev [7] and a later one by Green [8]. Green shows how one can deduce macroscopic equations directly from (1.63) (by taking moments in velocity space). Kadomtsev's procedure is not quite as general as Green's, but it gives a better insight into the microscopic behavior of the system. In Sections 8 - 10 we shall therefore make a further study of the implications of equation (1.63) along the general lines of presentation of Kadomtsev, showing how the usual Boltzmann equation can be deduced from equation (1.63) (with a collision term differing somewhat from the usual ones). Unlike Kadomtsev, however, we shall allow magnetic fields that vary in time, our equilibrium conditions (1.57) are more general than his, and our results are in part valid for a less restricted system.

Later on, when we deduce the macroscopic equations from Boltzmann's equation we shall occasionally have the opportunity to make comparisons with the results of Green.

Our system is now a binary mixture of electrons (index 1) and positive ions (index 2), and we suppose that the assumption (1.23), stating that the electrostatic interaction energy of the particles is much smaller than their kinetic energy, is correct,

$$e^2/d \ll \frac{1}{2} \quad \text{or} \quad 1 \ll nD^3 . \quad (1.64)$$

In this case all correlation factors  $\varphi$  are small quantities, while the triple correlation  $\varphi_{\alpha\beta\gamma}$  is smaller than the binary factor  $\varphi_{\alpha\beta}$  by one order of magnitude, and may be neglected.

The problem is now to find  $\varphi_{\alpha\beta}$ . We can derive the equation to determine  $\varphi_{\alpha\beta}$  in the following manner:

We write down Liouville's equation (1.3) for  $F_\alpha(\mathbf{r}, \mathbf{c}, t)$  and for  $F_\beta(\mathbf{r}', \mathbf{c}', t')$ . We multiply the first equation by  $F'_\beta$  and the second by  $F_\alpha$ , add and average. In this manner we obtain an equation for  $f_{\alpha\beta}$  which contains  $f_{\alpha\beta\gamma}$ ,

$$\begin{aligned} & \frac{df_{\alpha\beta}}{dt} + \mathbf{c} \cdot \frac{df_{\alpha\beta}}{d\mathbf{r}} + \mathbf{c}' \cdot \frac{df_{\alpha\beta}}{d\mathbf{r}'} + \mathbf{F}_{\alpha 0} \cdot \frac{df_{\alpha\beta}}{d\mathbf{c}} + \mathbf{F}'_{\beta 0} \cdot \frac{df_{\alpha\beta}}{d\mathbf{c}'} + \\ & + \mathbf{F}_{\alpha\beta} \cdot \frac{df_{\alpha\beta}}{d\mathbf{c}} + \mathbf{F}'_{\beta\alpha} \cdot \frac{df_{\alpha\beta}}{d\mathbf{c}'} + \\ & + \frac{d}{d\mathbf{c}} \cdot \sum_\gamma \int \mathbf{F}_{\alpha\gamma} f_{\alpha\beta\gamma} d\mathbf{r}'' d\mathbf{c}'' + \frac{d}{d\mathbf{c}'} \cdot \sum_\gamma \int \mathbf{F}'_{\beta\gamma} f_{\alpha\beta\gamma} d\mathbf{r}'' d\mathbf{c}'' = 0 . \end{aligned} \quad (1.65)$$

$\mathbf{F}_{\alpha\beta} = \frac{e_\alpha}{m_\alpha} (\mathbf{E}_\beta + \frac{1}{c} \mathbf{c} \times \mathbf{B}_\beta)$  is, as before, the force per unit mass on a particle  $\alpha$  at the "point"  $(\mathbf{r}, \mathbf{c})$  due to a particle  $\beta$  at the "point"  $(\mathbf{r}', \mathbf{c}')$ .

In this equation we substitute the expressions (1.60) and (1.61) for  $f_{\alpha\beta}$  and  $f_{\alpha\beta\gamma}$  and, using equation (1.62), obtain:

$$\begin{aligned}
 & \frac{d\varphi_{\alpha\beta}(\mathbf{r}, \mathbf{e}, \mathbf{r}', \mathbf{e}', t)}{dt} + \mathbf{e} \cdot \frac{d\varphi_{\alpha\beta}}{d\mathbf{r}} + \mathbf{e}' \cdot \frac{d\varphi_{\alpha\beta}}{d\mathbf{r}'} + \mathbf{F}_{\alpha} \cdot \frac{d\varphi_{\alpha\beta}}{d\mathbf{e}} + \\
 & + \mathbf{F}'_{\beta} \cdot \frac{d\varphi_{\alpha\beta}}{d\mathbf{e}'} + \mathbf{F}_{\alpha\beta} \cdot \frac{df_{\alpha}}{d\mathbf{e}} f'_{\beta} + \mathbf{F}'_{\beta\alpha} \cdot f_{\alpha} \frac{df'_{\beta}}{d\mathbf{e}'} = \\
 & = - \mathbf{F}_{\alpha\beta} \cdot \frac{d\varphi_{\alpha\beta}}{d\mathbf{e}} - \mathbf{F}'_{\beta\alpha} \cdot \frac{d\varphi_{\alpha\beta}}{d\mathbf{e}'} \\
 & - \frac{df_{\alpha}}{d\mathbf{e}} \cdot \sum_{\gamma} \int \mathbf{F}_{\alpha\gamma} \varphi_{\beta\gamma}(\mathbf{r}', \mathbf{e}', \mathbf{r}'', \mathbf{e}'', t) d\mathbf{r}'' d\mathbf{e}'' \\
 & - \frac{df'_{\beta}}{d\mathbf{e}'} \cdot \sum_{\gamma} \int \mathbf{F}'_{\beta\gamma} \varphi_{\alpha\gamma}(\mathbf{r}, \mathbf{e}, \mathbf{r}'', \mathbf{e}'', t) d\mathbf{r}'' d\mathbf{e}'' .
 \end{aligned} \tag{1.66}$$

Equation (1.66) is very complicated and must be solved by methods of approximation. We first require that the equation be satisfied in the stationary case ( $\frac{d}{dt} = 0$ ) by substitution of the quantities

$$\begin{aligned}
 f_{\alpha}^{(0)} &= n_{\alpha} \left( \frac{m_{\alpha}}{2\pi\hbar} \right)^{3/2} \exp \left( - \frac{m_{\alpha}(\mathbf{e} - \mathbf{e}_0)^2}{2\hbar} \right) , \\
 \varphi_{\alpha\beta}^{(0)} &= f_{\alpha}^{(0)} f_{\beta}^{(0)} \chi_{\alpha\beta}(|\mathbf{r} - \mathbf{r}'|) , \quad \chi_{\alpha\beta} = \chi_{\beta\alpha} .
 \end{aligned} \tag{1.67}$$

We next require that in this case the equilibrium conditions (2.91), to be deduced later, are valid. These equilibrium conditions differ from those adopted by Kadomtsev by allowing spatial gradients and a mean velocity field  $\mathbf{e}_0 \neq 0$ .

Our next step is a transformation of variables in equation (1.66) from the set  $(\mathbf{r}, \mathbf{e}, \mathbf{r}', \mathbf{e}', t)$  to the set  $(\mathbf{r}, \mathbf{C}, \mathbf{r}', \mathbf{C}', t)$ , where  $\mathbf{C} = \mathbf{e} - \mathbf{e}_0$ ,  $\mathbf{C}' = \mathbf{e}' - \mathbf{e}_0$ . On inserting the expressions (1.67) into equation (1.66) we obtain, after some simplifications, an expression which is a polynomial of the second degree in  $\mathbf{C}$  and  $\mathbf{C}'$ . The constant term and the coefficients of the second-order terms disappear when the equilibrium conditions (2.91) are introduced. This is also the case for a part of the first-order coefficients. The remaining part must also disappear, and we are left with the equation

$$\begin{aligned}
 & \frac{d\chi_{\alpha\beta}}{d\mathbf{r}} - \frac{e_{\alpha} e_{\beta}}{\hbar} \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} = \\
 & = \frac{e_{\alpha} e_{\beta}}{\hbar} \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \chi_{\alpha\beta} + \sum_{\gamma} \frac{e_{\alpha} e_{\beta}}{\hbar} \int \frac{\mathbf{r} - \mathbf{r}''}{|\mathbf{r} - \mathbf{r}''|^3} \chi_{\beta\gamma} n''_{\gamma} d\mathbf{r}'' .
 \end{aligned} \tag{1.68}$$

On putting  $-e_1 = e_2 = e$ ,  $n_1 = n_2 = n$ , Kadomtsev's equation results. This equation is therefore valid for more general equilibrium conditions than those adopted by Kadomtsev.

Putting in equation (1.68)  $\mathbf{r} - \mathbf{r}' = \mathbf{q}$ ,  $\mathbf{r}'' - \mathbf{r}' = \mathbf{q}'$ , the equation takes the form

$$\begin{aligned} \frac{d\chi_{\alpha\beta}(q)}{dq} - \frac{e_{\alpha}e_{\beta}}{\mathfrak{z}} q/q^3 = \frac{e_{\alpha}e_{\beta}}{\mathfrak{z}} q/q^3 \chi_{\alpha\beta}(q) + \\ + \sum_{\gamma} \frac{e_{\alpha}e_{\gamma}n}{\mathfrak{z}} \int \frac{q-q'}{|q-q'|^3} \chi_{\beta\gamma}(q') dq' \end{aligned} \quad (1.69)$$

For distances  $q$  greater than the distance  $q_0 \sim e^2/\mathfrak{z}$  corresponding to a mean deflection  $\pi/2$  of the particles when they collide, we can neglect the first term on the right-hand side of equation (1.69). The resulting equation is easily integrated, giving

$$\chi_{\alpha\beta}(q) + \sum_{\gamma} \frac{e_{\alpha}e_{\gamma}n}{\mathfrak{z}} \int \frac{1}{|q-q'|} \chi_{\beta\gamma}(q') dq' = - \frac{e_{\alpha}e_{\beta}}{\mathfrak{z}} \frac{1}{q} \quad (1.70)$$

We have shown that the arguments of Kadomtsev may so far be extended to a more general situation. As the further computations are lacking, we shall nevertheless be satisfied only to give the results of Kadomtsev. We must expect, however, to get similar results even in the more general case.

Assuming with Kadomtsev that  $-e_1 = e_2 = e$ ,  $n_1 = n_2 = n$ , (electrical neutrality) the solution of equation (1.70) is given by

$$\chi_{\alpha\beta}(q) = \frac{e_{\alpha}e_{\beta}}{\mathfrak{z}} \frac{1}{q} e^{-\beta/D} \quad (1.71)$$

where  $D$  is the Debye shielding distance,

$$D = \left( \frac{\mathfrak{z}}{8\pi e^2 n} \right)^{\frac{1}{2}} \quad (1.72)$$

and at distances greater than  $D$  the correlation between the particles will rapidly approach zero. The condition (1.64),  $q_0 = e^2/\mathfrak{z} \ll d$ , means

that the region where the solution (1.71) is not valid,  $q \lesssim \frac{e^2}{\mathfrak{z}}$ , constitutes a very small part of the total correlation region. We shall therefore not worry about the form of the solution within this region, but simply neglect the effect of collisions with impact parameter less than  $q_0$ . This is equivalent to neglecting the short-range collisions (Section 4), and entails that the first two terms on the right-hand side of equation (1.60) may be dropped.

We shall further assume that the deviations in the state from the equilibrium conditions (1.67) are slight. We may then insert the expression  $\varphi_{\alpha\beta}$  (1.71) into the right-hand side of equation (1.66) which is small in terms of  $1/nD^3$ , and also into the terms on the left-hand side involving the macroscopic forces. We write these terms as the sum of a part symmetrical and a part antisymmetrical in  $\mathbf{q} = \mathbf{r} - \mathbf{r}'$ , and correspondingly split  $\varphi_{\alpha\beta}$  into two parts

$$\varphi_{\alpha\beta} = \varphi_{\alpha\beta}^{(+)} + \varphi_{\alpha\beta}^{(-)} \quad (1.73)$$

$\varphi_{\alpha\beta}^{(+)}$  and  $\varphi_{\alpha\beta}^{(-)}$  are then defined by

$$\frac{d\varphi_{\alpha\beta}^{(+)}}{dt} + c \cdot \frac{d\varphi_{\alpha\beta}^{(+)}}{d\mathbf{r}} + c' \cdot \frac{d\varphi_{\alpha\beta}^{(+)}}{d\mathbf{r}'} = -\frac{1}{\beta} \left[ \frac{m_\alpha}{\beta} c \cdot \mathbf{F}_\alpha + \frac{m_\beta}{\beta} c' \cdot \mathbf{F}'_\beta \right] f_\alpha f'_\beta U(q), \quad (1.74)$$

$$\frac{d\varphi_{\alpha\beta}^{(-)}}{dt} + c \cdot \frac{d\varphi_{\alpha\beta}^{(-)}}{d\mathbf{r}} + c' \cdot \frac{d\varphi_{\alpha\beta}^{(-)}}{d\mathbf{r}'} = \left[ \frac{1}{m_\alpha} \frac{df_\alpha}{dc} f'_\beta - \frac{1}{m_\beta} f_\alpha \frac{df'_\beta}{dc'} \right] \frac{d}{d\mathbf{r}} U(q), \quad (1.75)$$

where  $U(q) = -e^2/q e^{-q/D}$ ,  $q = |\mathbf{r} - \mathbf{r}'|$ .

What is now left is to solve the equations (1.74) and (1.75) and insert the resulting expression (1.73) into equation (1.63). The form of this equation is then determined.

The contribution to equation (1.63) from the symmetrical part  $\varphi_{\alpha\beta}^{(+)}$  may be considered as a correction to the macroscopic force field. This correction has the form

$$f_\alpha \Delta F_\alpha = \sum_\beta \frac{e_\alpha e_\beta}{m_\alpha} \int \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \varphi_{\alpha\beta}^{(+)} d\mathbf{r}' d\mathbf{c}', \quad (1.76)$$

and is in general a function of  $\mathbf{r}$ ,  $\mathbf{c}$  and  $t$ .

In a similar way the antisymmetric part  $\varphi_{\alpha\beta}^{(-)}$  will give a contribution

$$-\frac{d}{dt} f_\alpha = \sum_\beta \frac{e_\alpha e_\beta}{m_\alpha} \frac{d}{dc} \cdot \int \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \varphi_{\alpha\beta}^{(-)} d\mathbf{r}' d\mathbf{c}' \quad (1.77)$$

to the equation. This contribution we define as the collision term.

It is worth noting that both the correction  $\Delta F_\alpha$  and the collision term  $-\frac{d}{dt} f_\alpha$  will vanish when the correlation between the particles, represented by  $\varphi_{\alpha\beta}$ , vanishes.

## 9. THE CORRECTION TO THE MACROSCOPIC FIELD

We shall not carry out the detailed solution of equation (1.74) as has been done by Kadomtsev. His results may be summarized in the following remark.

The existence of the correction term  $\Delta F_\alpha$  may be explained physically by the formation around each gas particle of a correlated "cloud" of particles of opposite charge and dimensions  $\sim D^3$ . In the case  $\mathbf{E} = \mathbf{B} = 0$  the particle cloud will be spherically symmetrical, but when  $\mathbf{E} \neq 0$  the "polarization"  $\Delta F_\alpha$  will make itself noticed. When the magnetic field is weak, the polarization will be along  $\sim \mathbf{E}$ , while in the opposite case the displacement of the correlated cloud and the polarization will be along the strong magnetic field. The gas thus behaves like a dielectric medium.

The "polarization"  $\Delta F_\alpha$  is, however, proportional to  $1/nD^3$  and maybe

neglected when terms of this order of magnitude are unimportant. For real gases, on the other hand, where the interaction energy is not negligible, the "virial term"  $\Delta F_\alpha$  plays an important role.

## 10. THE COLLISION TERM

We now try to solve equation (1.75) for  $\varphi_{\alpha\beta}^{(-)}$ , in order to find  $\frac{d f_\alpha}{dt}$  by substitution in equation (1.77).

We assume that the distribution functions  $f_\alpha = f_\alpha(\mathbf{r}, \mathbf{c}, t)$  do not vary appreciably in the correlation region ( $\sim D^3$ ), and moreover that they are approximatively constant during the time used by a particle to cross this region (on the average), we may neglect the dependence in time and position for  $f_\alpha$ , i.e.  $f_\alpha = f_\alpha(\mathbf{c})$ . We further assume the following form for  $\varphi_{\alpha\beta}^{(-)}$ ,

$$\varphi_{\alpha\beta}^{(-)} = \varphi_{\alpha\beta}^{(-)}(\mathbf{r} - \mathbf{r}', \mathbf{c}, \mathbf{c}') . \quad (1.78)$$

Equation (1.75) then takes the form

$$(\mathbf{c} - \mathbf{c}') \cdot \frac{d \varphi_{\alpha\beta}^{(-)}}{d \mathbf{q}} = \left( \frac{1}{m_\alpha} \frac{d f_\alpha}{d \mathbf{c}} f'_\beta - \frac{1}{m_\beta} f_\alpha \frac{d f'_\beta}{d \mathbf{c}'} \right) \cdot \frac{d}{d \mathbf{q}} U(q) . \quad (1.79)$$

The next step is to introduce cylindrical coordinates, so that the coordinates for  $\mathbf{q}$  are  $(r, \varphi, z)$ . The  $z$ -axis is chosen along the vector  $\mathbf{c} - \mathbf{c}'$ . We then get

$$\frac{d}{dz} \varphi_{\alpha\beta}^{(-)}(r, \varphi, z, \mathbf{c}, \mathbf{c}') = \left[ \frac{1}{m_\alpha} \frac{d f_\alpha}{d \mathbf{c}} f'_\beta - \frac{1}{m_\beta} f_\alpha \frac{d f'_\beta}{d \mathbf{c}'} \right] \cdot \frac{\frac{d}{d \mathbf{q}} U(\sqrt{q^2 + z^2})}{|\mathbf{c} - \mathbf{c}'|} , \quad (1.80)$$

which can be immediately integrated, giving

$$\varphi_{\alpha\beta}^{(-)} = \left[ \frac{1}{m_\alpha} \frac{d f_\alpha}{d \mathbf{c}} f'_\beta - \frac{1}{m_\beta} f_\alpha \frac{d f'_\beta}{d \mathbf{c}'} \right] \cdot \frac{d}{d \mathbf{q}} \int_{-\infty}^z \frac{U(\sqrt{q^2 + \xi^2})}{|\mathbf{c} - \mathbf{c}'|} d\xi . \quad (1.81)$$

We have then assumed that  $\varphi_{\alpha\beta}^{(-)} = 0$  for  $z = -\infty$ . We now substitute  $\varphi_{\alpha\beta}^{(-)}$  in equation (1.77), getting the final expression for the collision term,

$$\frac{d f_\alpha}{dt} = \sum_\beta \frac{2\pi\lambda e_\alpha^2 e_\beta^2}{m_\alpha} \frac{d}{d \mathbf{c}} \cdot \int U \cdot \left[ \frac{f'_\beta}{m_\alpha} \frac{d f_\alpha}{d \mathbf{c}} - \frac{f_\alpha}{m_\beta} \frac{d f'_\beta}{d \mathbf{c}} \right] d\mathbf{c}' . \quad (1.82)$$

This is the collision term on Landau's form, given in equation (1.27). This term has been the subject of some controversies in scientific literature. Enoch [9] has recently proved the equivalence of the Landau collision term to the Fokker-Planck term on the assumption that binary correlations dominate.

With this collision term equation (1.63) takes the form

$$\frac{\partial f_{\alpha}}{\partial t} + \mathbf{v} \cdot \frac{\partial f_{\alpha}}{\partial \mathbf{r}} + \frac{\partial}{\partial \mathbf{v}} \cdot (f_{\alpha} \mathbf{F}_{\alpha}^{\text{eff}}) = \frac{\partial f_{\alpha}}{\partial t} , \quad (1.83)$$

where

$$\mathbf{F}_{\alpha}^{\text{eff}} = \mathbf{F}_{\alpha} + \Delta \mathbf{F}_{\alpha} .$$

In the case  $1 \ll nD^3$  we neglect  $\Delta \mathbf{F}_{\alpha}$ , and equation (1.83) gives us Boltzmann's kinetic equation (1.9).

\* \* \*

## PART II. RELAXATION PHENOMENA AND EQUILIBRIUM STATE

### 11. THE H-THEOREM AND THE TENDENCY TOWARDS STATISTICAL EQUILIBRIUM

When we consider the statistical state of a system, the molecular interactions are of decisive importance. Their significance has been clearly stated by Fowler [10]:

"Any possible mechanism (of interaction) left to act by itself must set up and preserve the laws of statistical equilibrium."

The so-called H-theorem for gases was first proposed by Boltzmann in 1872 [11]. It stated that, when left to itself without interaction with the environment, a gas would approach statistical equilibrium represented by a Maxwellian distribution function, as a result of binary collisions among the molecules ( $E$  is the sum of kinetic and potential energy,  $E = \frac{1}{2} mc^2 + m\phi$ ),

$$f = n \left( \frac{m\beta}{2\pi} \right)^{3/2} e^{-\beta E}, \quad \beta = 1/kT. \quad (2.1)$$

This distribution was earlier found by Maxwell in 1860, but at the time his proof was not considered satisfactory.

The point of departure for Boltzmann's proof of the H-theorem and the subsequent improvement on the theorem was Boltzmann's equation.

In the Maxwell-Boltzmann statistics the thermodynamic "probability" for a system is given by

$$W = N! \prod_i \frac{G_i^{N_i}}{N_i!}, \quad (2.2)$$

where  $N_i$  is the population number and  $G_i$  the statistical "weight" of the  $i$ -th phase cell in the six-dimensional phase space, while  $N = \sum_i N_i$  is the total number of molecules. We assume  $W$  to have an increasing tendency, and  $W = W_{\max}$  or  $\delta W = 0$  characterize statistical equilibrium. The latter quantities are distinguished by Boltzmann's law of distribution.

$$\frac{N_i}{G_i} = \frac{1}{Z} e^{-\beta E_i}, \quad \beta = 1/kT, \quad (2.3)$$

where  $E_i$  is the energy level of the  $i$ -th cell, and the "sum of state"

$$Z = \sum_i G_i e^{-\beta E_i}.$$

In this state the thermodynamic expression for the entropy is given by  $S = \ln W$  ( $k$  is Boltzmann's constant).

scopic quantities. What interests us is to find the *microscopic justification* of those assumptions. We have so far merely assumed that the thermodynamic probability of a system has a growing tendency, with the result that our system approaches the state of equilibrium. With the aid of Boltzmann's kinetic equation we can now directly show that because of the interaction between the molecular systems the function  $H$  will decrease towards a lower, negative limit which corresponds to thermodynamic and statistical equilibrium. (The existence of this lower limit has been proved by Chapman and Cowling [4].) The state is then stationary with a Maxwellian distribution function, and the entropy  $S_{\text{max}} = -kH_{\text{min}}$  corresponds to the classic thermodynamic entropy. This is the substance of Boltzmann's H-theorem.

## 12. PROOF OF THE H-THEOREM

According to the definition (2.9) the time variation of  $H_\alpha$  is given by the expression

$$\frac{\partial H_\alpha}{\partial t} = \int (1 + \ln f_\alpha) \frac{\partial f_\alpha}{\partial t} d\mathbf{c} \quad (2.10)$$

in which we substitute for  $\frac{\partial f_\alpha}{\partial t}$  from equation (1.83) and rearrange, getting

$$\frac{\partial H_\alpha}{\partial t} = \frac{\partial_c H_\alpha}{\partial t} - \frac{\partial}{\partial \mathbf{r}} \cdot \int \mathbf{c} f_\alpha \ln f_\alpha d\mathbf{c} + \int \left( \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{F}_\alpha^{\text{eff}} \right) f_\alpha \ln f_\alpha d\mathbf{c} \quad (2.11)$$

or

$$\frac{\partial H_\alpha}{\partial t} = \frac{\partial_c H_\alpha}{\partial t} - \frac{\partial}{\partial \mathbf{r}} \cdot (\overline{n_\alpha \mathbf{c} \ln f_\alpha}) + \overline{n_\alpha \left( \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{F}_\alpha^{\text{eff}} \right) \ln f_\alpha} \quad (2.12)$$

Here  $\frac{\partial_c H_\alpha}{\partial t}$  is the change in  $H_\alpha$  because of the molecular interactions

( $\int \frac{\partial_c f_\alpha}{\partial t} d\mathbf{c} = 0$ , see Appendix),

$$\frac{\partial_c H_\alpha}{\partial t} = \int (1 + \ln f_\alpha) \frac{\partial_c f_\alpha}{\partial t} d\mathbf{c} = n_\alpha \frac{\partial_c \overline{\ln f_\alpha}}{\partial t} \quad (2.13)$$

If we write

$$\frac{\partial H_\alpha}{\partial t} + \frac{\partial}{\partial \mathbf{r}} \cdot (\overline{n_\alpha \mathbf{c} \ln f_\alpha}) = \frac{\partial_c H_\alpha}{\partial t} + \overline{n_\alpha \left( \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{F}_\alpha^{\text{eff}} \right) \ln f_\alpha} \quad (2.14)$$

this may be interpreted as an equation of continuity for the "entropy density"  $H_\alpha$ . This equation also follows from equation (1.57) by setting  $\Phi_\alpha = \ln f_\alpha$ . The vector  $\overline{n_\alpha \mathbf{c} \ln f_\alpha} = \int \mathbf{c} f_\alpha \ln f_\alpha d\mathbf{c}$  is the "entropy flow density", and the right-hand side of equation (2.14) is the "entropy source density".

As shown elsewhere (Section 8) the effective macroscopic field  $\mathbf{F}_\alpha^{\text{eff}}$  which includes  $\Delta \mathbf{F}_\alpha$  may be a function of  $\mathbf{c}$ . We can therefore not imme-



There is no thermodynamic definition of entropy for non-uniform and non-stationary states, but it is convenient to choose the equation

$$S = k \ln W \quad (2.4)$$

as an *equation of definition* even in this case,  $W$  being defined for all states. This procedure seems natural as both  $W$  and  $S$  are assumed to have increasing tendency, and because the entropy for thermodynamic systems is additive, while the thermodynamic "probability" is multiplicative. (This argument has been criticized by Fowler [10].)

If we use the expression (2.4) for  $W$  and Stirling's formula

$$\ln N! \approx N \ln N - N,$$

we can easily deduce that

$$\ln W \approx - \sum_i \left( \frac{N_i}{G_i} \ln \frac{N_i}{G_i} \right) G_i + N \ln N. \quad (2.5)$$

The statistical "weight"  $G_i$  is by definition proportional to the volume of the  $i$ -th phase cell  $\Delta\phi_i$ . If we choose the proportionality factor equal to unity and let  $\Delta\phi_i \rightarrow h^3$  ( $h$  is Planck's constant), the average density of particles in the phase cell,

$$\frac{N_i}{G_i} \rightarrow \frac{\Delta N_i}{\Delta\phi_i},$$

approaches a limit  $f$ , and the sum (2.5) can be replaced by an integral,

$$\ln W \approx - \int f \ln f d\phi + \text{Const.}, \quad d\phi = dr d\epsilon. \quad (2.6)$$

Our expression (2.4) for the generalized entropy thus becomes

$$S = S(t) = -k \int f \ln f d\phi + \text{Const.} \quad (2.7)$$

If we have a composite gas, we define the entropy as the sum of the entropies of the different components of the gas ( $\alpha = 1, 2, \dots$ ),

$$S = \sum_{\alpha} S_{\alpha}, \quad S_{\alpha} = -k \int f_{\alpha} \ln f_{\alpha} d\phi. \quad (2.8)$$

This corresponds to the total thermodynamic probability being equal to the product of all component probabilities.

Instead of  $S_{\alpha}$  it is customary to work with the functions  $H_{\alpha 0}$  or  $H_{\alpha}$ , defined by

$$H_{\alpha 0}(t) = \int H_{\alpha} dr, \quad H_{\alpha}(r, t) = \int f_{\alpha} \ln f_{\alpha} d\epsilon, \quad (2.9)$$

$$\text{i.e. } S_{\alpha} = -k H_{\alpha 0}.$$

Thus  $H$  is proportional to the negative entropy.

The distribution (2.1) now corresponds to the equilibrium distribution (2.3). This result, however, rests on several assumptions about macro-

diately put  $\frac{d}{dt} \cdot F_{\alpha}^{\text{eff}} = 0$ , even though the contribution from the Lorentz term  $\frac{e_{\alpha}}{m_{\alpha}} \mathbf{c} \times \mathbf{B}$  of course vanishes. This approximation is, however, permissible on the assumption  $nD^3 \gg 1$ , and the "entropy source density" is then completely due to the so-called collisions.

For the time variation of the negative entropy within a closed surface  $\Sigma$  we get the expression

$$\begin{aligned} \frac{dH_{\alpha 0}}{dt} &= - \int_V \frac{d}{dt} \cdot (n_{\alpha} \overline{c \ln f_{\alpha}}) d\mathbf{r} + \int_V \frac{d_c H_{\alpha}}{dt} d\mathbf{r} = \\ &= - \int_{\Sigma} n_{\alpha} \overline{c \ln f_{\alpha}} dS + \int_V \frac{d_c H_{\alpha}}{dt} d\mathbf{r} . \end{aligned} \quad (2.15)$$

If the first contribution disappears, we are left with the change in  $H_{\alpha 0}$  due to collisions,

$$\frac{dH_{\alpha 0}}{dt} = \int \frac{d_c H_{\alpha}}{dt} d\mathbf{r} , \quad \frac{d_c H_{\alpha}}{dt} = n_{\alpha} \frac{d_c \overline{\ln f_{\alpha}}}{dt} . \quad (2.16)$$

Our problem is now to show that collisions can only lead to  $\frac{dH_{\alpha 0}}{dt} \leq 0$ , where the equality sign is valid when the state of equilibrium is attained.

We have seen earlier that collisions in ionized gases must be divided into binary or short-range collisions, and multiple or long-range collisions. The validity of the H-theorem, on the conditions that collisions are binary, was first proved by Boltzmann [11]. More unassailable proofs were later given by Lorentz [12], Jeans [13], Fowler [10] and others, both for a simple and a composite gas.

The procedure of these authors is substantially that described by Chapman and Cowling [4], and consists in substituting the two-particle collision integral (1.26) in expression (2.16) for  $\frac{d_c f_{\alpha}}{dt}$ , and, using certain transformations, showing that the following relation is valid,

$$\frac{d_c H_{\alpha}}{dt} \leq 0 . \quad (2.17)$$

It is further shown that the equation  $\frac{d_c H_{\alpha}}{dt} = 0$  and detailed balancing (i.e. the quantity  $f_{\alpha} f_{\beta}$  is unaltered by collisions between particles of the types  $\alpha$  and  $\beta$ ), can only be valid for a Maxwellian distribution function.

In these treatments, however, the effect of long-range forces of ionized molecules has not been taken into account. This we now want to do.

We shall show that the H-theorem remains valid provided that we let the molecular interactions be represented by the collision term on Landau's form.

Consider an ionized gas, composed of several components ( $\alpha = 1, 2, \dots$ ) with distribution functions  $f_{\alpha}(\mathbf{r}, \mathbf{c}, t)$  particle masses  $m_{\alpha}$  and

particle charge  $e_\alpha$ . The collision term  $\frac{\partial f_\alpha}{\partial t}$  is the sum of all contributions  $\left(\frac{\partial f_\alpha}{\partial t}\right)_\beta$ , contributing to the change in  $f_\alpha$  from collisions with particles  $\beta$ . According to (1.82)

$$\left(\frac{\partial f_\alpha}{\partial t}\right)_\beta = - \frac{2\pi\lambda e_\alpha^2 e_\beta^2}{m_\alpha} \frac{\partial}{\partial c} \cdot \int \mathbf{U} \cdot \left( \frac{f_\alpha}{m_\beta} \frac{\partial f'_\beta}{\partial c'} - \frac{f'_\beta}{m_\alpha} \frac{\partial f_\alpha}{\partial c} \right) d\mathbf{c}', \quad (2.18)$$

where  $f'_\beta = f_\beta(\mathbf{c}')$ .

The total negative entropy per unit volume is

$$H = \sum H_\alpha = \int f_\alpha \ln f_\alpha d\mathbf{c}.$$

For  $\left(\frac{\partial H_\alpha}{\partial t}\right)_\beta$  we get  $(k_{\alpha\beta} = 2\pi\lambda e_\alpha^2 e_\beta^2)$ ,

$$\begin{aligned} \left(\frac{\partial H_\alpha}{\partial t}\right)_\beta = & - \frac{k_{\alpha\beta}}{m_\alpha} \int d\mathbf{c} \ln f_\alpha \frac{\partial}{\partial c} \cdot \int \mathbf{U} \cdot \left( \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial c'} - \right. \\ & \left. - \frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial c} \right) f_\alpha f'_\beta d\mathbf{c}'. \end{aligned} \quad (2.19)$$

We introduce the following abbreviations,

$$V_{\alpha\beta} = V_{\alpha\beta}(\mathbf{c}, \mathbf{c}') = \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial c'} - \frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial c}$$

and

(2.20)

$$A_{\alpha\beta} = A_{\alpha\beta}(\mathbf{c}) = \int \mathbf{U} \cdot V_{\alpha\beta} f_\alpha f'_\beta d\mathbf{c}',$$

i.e.

$$\begin{aligned} \left(\frac{\partial H_\alpha}{\partial t}\right)_\beta = & - \frac{k_{\alpha\beta}}{m_\alpha} \int \ln f_\alpha \frac{\partial}{\partial c} \cdot A_{\alpha\beta} d\mathbf{c} = \\ = & - \frac{k_{\alpha\beta}}{m_\alpha} \int \frac{\partial}{\partial c} \cdot (\ln f_\alpha A_{\alpha\beta}) d\mathbf{c} + \frac{k_{\alpha\beta}}{m_\alpha} \int A_{\alpha\beta} \cdot \frac{\partial}{\partial c} \ln f_\alpha d\mathbf{c}. \end{aligned} \quad (2.21)$$

But as  $A_{\alpha\beta}$  is proportional to  $f_\alpha$  (2.20), the first integral in equation (2.21) must vanish (assuming that  $f_\alpha \rightarrow 0$  when  $|\mathbf{c}| \rightarrow \infty$ ), and we are left with

$$\left(\frac{\partial H_\alpha}{\partial t}\right)_\beta = \frac{k_{\alpha\beta}}{m_\alpha} \int A_{\alpha\beta}(\mathbf{c}) \cdot \frac{\partial \ln f_\alpha}{\partial c} d\mathbf{c},$$

or

(2.22)

$$\left(\frac{\partial H_\alpha}{\partial t}\right)_\beta = k_{\alpha\beta} \int d\mathbf{c} \int d\mathbf{c}' f_\alpha f'_\beta \frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial c} \cdot \mathbf{U} \cdot V_{\alpha\beta}(\mathbf{c}, \mathbf{c}').$$

For  $\left(\frac{\partial_c H_\beta}{\partial t}\right)_\alpha$  we get in a completely analogous manner,

$$\left(\frac{\partial_c H_\beta}{\partial t}\right)_\alpha = k_{\beta\alpha} \int d\mathbf{c} \int d\mathbf{c}' f_\beta f'_\alpha \frac{1}{m_\beta} \frac{\partial \ln f_\beta}{\partial \mathbf{c}} \cdot \mathbf{U} \cdot \mathbf{V}_{\beta\alpha}(\mathbf{c}, \mathbf{c}') . \quad (2.23)$$

The value of the integral does not change if we switch about the primed and the non-primed quantities,

$$\left(\frac{\partial_c H_\beta}{\partial t}\right)_\alpha = k_{\beta\alpha} \int d\mathbf{c}' \int d\mathbf{c} f'_\beta f_\alpha \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial \mathbf{c}'} \cdot \mathbf{U} \cdot \mathbf{V}_{\beta\alpha}(\mathbf{c}', \mathbf{c}) . \quad (2.24)$$

The order of integration may also be changed,

$$\begin{aligned} \left(\frac{\partial_c H_\beta}{\partial t}\right)_\alpha &= k_{\beta\alpha} \int d\mathbf{c} \int d\mathbf{c}' f'_\beta f_\alpha \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial \mathbf{c}'} \cdot \mathbf{U} \cdot \mathbf{V}_{\beta\alpha}(\mathbf{c}', \mathbf{c}) = \\ &= k_{\alpha\beta} \int d\mathbf{c} \int d\mathbf{c}' f_\alpha f'_\beta \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial \mathbf{c}'} \cdot \mathbf{U} \cdot \mathbf{V}_{\beta\alpha}(\mathbf{c}', \mathbf{c}) . \end{aligned} \quad (2.25)$$

By summation of equations (2.22) and (2.25) we get, using the relation

$$\mathbf{V}_{\beta\alpha}(\mathbf{c}', \mathbf{c}) = -\mathbf{V}_{\alpha\beta}(\mathbf{c}, \mathbf{c}') , \quad (2.26)$$

that

$$\left(\frac{\partial_c H_\alpha}{\partial t}\right)_\beta + \left(\frac{\partial_c H_\beta}{\partial t}\right)_\alpha = -k_{\alpha\beta} \int d\mathbf{c} \int d\mathbf{c}' f_\alpha f'_\beta \mathbf{V}_{\alpha\beta}(\mathbf{c}, \mathbf{c}') \cdot \mathbf{U} \cdot \mathbf{V}_{\alpha\beta}(\mathbf{c}', \mathbf{c}) , \quad (2.27)$$

and therefore also,

$$\left(\frac{\partial_c H_\alpha}{\partial t}\right)_\alpha = -\frac{k_{\alpha\alpha}}{2} \int d\mathbf{c} \int d\mathbf{c}' f_\alpha f'_\alpha \mathbf{V}_{\alpha\alpha}(\mathbf{c}, \mathbf{c}') \cdot \mathbf{U} \cdot \mathbf{V}_{\alpha\alpha}(\mathbf{c}, \mathbf{c}') . \quad (2.28)$$

As

$$\mathbf{U} = \frac{1}{u^3} (u^2 \mathbf{I} - \mathbf{u}\mathbf{u}), \quad \mathbf{u} = \mathbf{c} - \mathbf{c}' ,$$

the expression  $\mathbf{V} \cdot \mathbf{U} \cdot \mathbf{V}$  has the form

$$\begin{aligned} \mathbf{V} \cdot \mathbf{U} \cdot \mathbf{V} &= \frac{1}{u^3} [u^2 \cdot \mathbf{V} \cdot \mathbf{I} \cdot \mathbf{V} - (\mathbf{V} \cdot \mathbf{u})(\mathbf{u} \cdot \mathbf{V})] = \\ &= \frac{1}{u^3} [u^2 \mathbf{V}^2 - (\mathbf{u} \cdot \mathbf{V})^2] \geq 0 , \end{aligned} \quad (2.29)$$

and the expressions (2.27) and (2.28) are always negative. They equal zero only if  $\mathbf{u}$  and  $\mathbf{V}$  are parallel vectors.

We have thus proved the H-theorem even in the following case,

$$\frac{\partial_c H}{\partial t} = \sum_{\alpha} \frac{\partial_c H_{\alpha}}{\partial t} = \sum_{\alpha\beta} \frac{\partial_c H_{\alpha}}{\partial t} \beta = \frac{1}{2} \sum_{\alpha\beta} \left[ \frac{\partial_c H_{\alpha}}{\partial t} \beta + \frac{\partial_c H_{\beta}}{\partial t} \alpha \right] \leq 0. \quad (2.30)$$

These results must be interpreted in the following manner:

The entropy for each gas component  $\alpha$  always increases as a result of multiple interactions between the molecules of the components, and attains its maximum value when  $V_{\alpha\alpha} \parallel u$  (2.28),

$$\frac{1}{m_{\alpha}} \frac{\partial \ln f'_{\alpha}}{\partial c'} - \frac{1}{m_{\alpha}} \frac{\partial \ln f_{\alpha}}{\partial c} = \frac{1}{\theta_{\alpha}} u = \frac{1}{\theta_{\alpha}} (c - c') \quad (2.31)$$

for all  $c$  and  $c'$  ( $\alpha = 1, 2, \dots$ ).

We then have

$$\begin{aligned} \frac{1}{m_{\alpha}} \frac{\partial \ln f_{\alpha}}{\partial c} + \frac{1}{\theta_{\alpha}} c &= \frac{1}{m_{\alpha}} \frac{\partial \ln f'_{\alpha}}{\partial c'} + \frac{1}{\theta_{\alpha}} c' = \\ &= \text{Const.} = \frac{1}{\theta_{\alpha}} c_{\alpha 0}, \end{aligned} \quad (2.32)$$

and consequently

$$\frac{1}{m_{\alpha}} \frac{\partial \ln f_{\alpha}}{\partial c} = - \frac{1}{\theta_{\alpha}} (c - c_{\alpha 0}) \quad (2.33)$$

with the solution

$$f_{\alpha} = N_{\alpha} \exp \left[ - \frac{m_{\alpha}}{2\theta_{\alpha}} (c - c_{\alpha 0})^2 \right] \quad (\alpha = 1, 2, \dots). \quad (2.34)$$

The entropy for each gas component no longer grows as a result of the interactions between the molecules of the gas component when the function of state has become Maxwellian with temperature  $\theta_{\alpha}$  and mean velocity  $c_{\alpha 0}$ .

We easily verify that  $c_{\alpha 0}$  and  $\theta_{\alpha}$  are really the mean velocity and mean temperature of the molecules by requiring that equation (2.34) satisfy the conditions

$$\begin{aligned} n_{\alpha} &= \int f_{\alpha} dc, \quad n_{\alpha} c_{\alpha 0} = \int c f_{\alpha} dc, \\ \frac{3}{2} \theta_{\alpha} &= \int \frac{1}{2} m_{\alpha} (c - c_{\alpha 0})^2 f_{\alpha} dc. \end{aligned} \quad (2.35)$$

The first condition, the condition of normalization, moreover gives the familiar value  $N_{\alpha}$ ,

$$N_{\alpha} = n_{\alpha} \left( \frac{m_{\alpha}}{2\pi\theta_{\alpha}} \right)^{3/2}. \quad (2.36)$$

Here  $n_{\alpha}$  is the density of the molecules  $\alpha$ .

We further see that the entropy will no longer increase as a result of interactions between molecules  $\alpha$  and  $\beta$  of different types (2.27) when  $V_{\alpha\beta} \parallel u$ ,

$$\frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial c'} - \frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial c} = \frac{1}{\mathfrak{A}} u = \frac{1}{\mathfrak{A}} (c - c') \quad (2.37)$$

for all  $c$  and  $c'$ . We then have,

$$\frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial c} + \frac{1}{\mathfrak{A}} c = \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial c'} + \frac{1}{\mathfrak{A}} c' = \text{Const} = \frac{1}{\mathfrak{A}} c_0, \quad (2.38)$$

i.e.

$$\frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial c} = \frac{1}{\mathfrak{A}} (c - c_0), \quad (2.39)$$

which has the solution

$$f_\alpha = N_\alpha \exp\left(-\frac{m_\alpha}{2\mathfrak{A}} (c - c_0)^2\right) \quad (\alpha = 1, 2, \dots) \quad (2.40)$$

Thus the equilibrium distributions are once more Maxwellian, but in this case with the same temperature,  $\mathfrak{A}$ , and mean velocity,  $c_0$ , for all components of the gas.

Such a distribution (2.40) will simultaneously lead to  $\left(\frac{\partial_c H_\alpha}{\partial t}\right)_\alpha = 0$  (for all  $\alpha$ ), so that

$$\frac{\partial H}{\partial t} = \sum_\alpha \frac{\partial_c H_\alpha}{\partial t} = \sum_{\beta\alpha} \left(\frac{\partial_c H_\alpha}{\partial t}\right) = 0. \quad (2.41)$$

Equation (2.40) will thus give the form of the distribution functions in the ultimate state of equilibrium.

In a gas which is originally far removed from statistical equilibrium we must consequently expect the following development:

Encounters between identical particles will initially establish local equilibrium distributions for each gas component, each with its own temperature and mean velocity. Next, collisions between the different gases will lead to equalization, and in the ultimate state of equilibrium the components will have the same temperature and mean velocity. The exact time development can, of course, not be predicted without knowledge of the characteristic relaxation times of each of the equalizing processes mentioned.

These relaxation times will be more closely studied in the following section. In the special case that our ionized gas is a plasma consisting of electrons  $(e_1, m_1)$  and positive ions  $(e_2, m_2)$ , ( $m_1 \ll m_2$ ), we find that the proportionality between the times  $\tau_{\alpha\beta}$  for equalization of energy between the particles  $\alpha$  and  $\beta$  is

$$\tau_{11} : \tau_{22} : \tau_{21} : \tau_{12} \approx 1 : \sqrt{\frac{m_2}{m_1}} : \frac{m_2}{m_1} : \frac{m_2}{m_1} \quad (2.42)$$

The proportionality between the equalization times for momentum is

$$\tau_1^1 : \tau_2^2 : \tau_2^1 : \tau_1^2 \approx 1 : \sqrt{\frac{m_2}{m_1}} : \frac{m_2}{m_1} : 1 . \quad (2.43)$$

This makes it possible to consider a plasma as consisting of two *approximately independent* component gases, each with its own well-defined temperature equilibrium is established for each component much quicker than mutual equalization. This is especially the case for the light electrons.

### 13. CHARACTERISTIC TIMES FOR THE RELAXATION PROCESSES

In the preceding section we showed that long-range interactions of the type that will occur in ionized gases will make the system approach and attain statistical equilibrium.

This is a property we must ascribe to all possible molecular interaction mechanisms [10] and this is the microscopic explanation of the macroscopic assumptions that the entropy must always increase [Eq. (3.84)] .

All mechanisms of interaction are in this sense equivalent and unimportant as long as we only wish to describe states of equilibrium. If, on the other hand, we wish to describe the development of states that are not in statistical equilibrium, the types of interaction are highly important, as they determine the relaxation times of the different equalizing processes.

The characteristic times  $\tau_{\alpha\beta}$  and  $\tau_{\alpha}^{\beta}$  for equalization of energy and momentum between two groups of identical molecules  $\alpha$  and  $\beta$  may in principle be evaluated with the aid of the known expression for  $\left(\frac{\partial c f_{\alpha}}{\partial t}\right)_{\beta}$ .

The average changes in momentum and energy due to encounters for the molecules  $\alpha$  per unit time is, according to the transport equation (1.57), expressed in terms of the velocity  $\mathbf{C}_{\alpha}' = \mathbf{C}_{\alpha} - \mathbf{C}_{\alpha 0}$

$$\mathbf{R}_{\alpha} = n_{\alpha} \frac{\partial c}{\partial t} \overline{(m_{\alpha} \mathbf{C}_{\alpha}')}, \quad Q_{\alpha} = n_{\alpha} \frac{\partial c}{\partial t} \overline{\left(\frac{1}{2} m_{\alpha} \mathbf{C}_{\alpha}'^2\right)} . \quad (2.44)$$

They are composed of the contributions from collisions with the single component gases,

$$\mathbf{R}_{\alpha} = \sum_{\beta} \mathbf{R}_{\alpha\beta} , \quad Q_{\alpha} = \sum_{\beta} Q_{\alpha\beta} , \quad (2.45)$$

$$\mathbf{R}_{\alpha\beta} = \int m_{\alpha} \mathbf{C}_{\alpha}' \left(\frac{\partial c f_{\alpha}}{\partial t}\right)_{\beta} d\mathbf{c} , \quad Q_{\alpha\beta} = \int \frac{1}{2} m_{\alpha} \mathbf{C}_{\alpha}'^2 \left(\frac{\partial c f_{\alpha}}{\partial t}\right)_{\beta} d\mathbf{c} .$$

The quantities with identical indices,  $\alpha = \beta$ , vanish when the state of equilibrium is established for each component, i.e.  $\left(\frac{\partial c f_{\alpha}}{\partial t}\right)_{\alpha} = 0$ , while the quantities with different indices,  $\alpha \neq \beta$ , vanish only when all components have attained the same temperature and mean velocity.

According to (1.57) we get for the changes in the mean velocities  $c_{\alpha 0}$  and energies  $\Phi_{\alpha}$  because of collisions,

$$m_{\alpha} n_{\alpha} \frac{dc_{\alpha 0}}{dt} = R_{\alpha}, \quad \frac{3}{2} n_{\alpha} \frac{d\Phi_{\alpha}}{dt} = Q_{\alpha}. \quad (2.46)$$

If we can now find expressions for  $R_{\alpha}$  and  $Q_{\alpha}$  it is possible to determine the relaxation times for equalization of mean velocity and temperature on the basis of these equations.

Consider a gas composed of electrons and positive ions with masses  $m_1$  and  $m_2$ . The effect of the collisions may be represented by Landau's collision integral (1.82). We first assume that each component gas is in the state of equilibrium at different values of  $c_{\alpha 0}$  and  $\Phi_{\alpha}$ , so that

$$R_{\alpha} = R_{\alpha\beta}, \quad Q_{\alpha} = Q_{\alpha\beta}, \quad \alpha \neq \beta.$$

Approximate expressions for these quantities may be found by taking into account that the mass of the electron is much smaller than the mass of the ion,  $m_1 \ll m_2$ , and that the thermal velocity of the electrons is much greater than that of the ions, provided that  $\Phi_1$  and  $\Phi_2$  are of the same order of magnitude. We also assume that the difference between the average velocities,  $u_0 = c_{10} - c_{20}$ , is small when compared to the electron velocity.

The tensor  $U$  in the collision integral depends on the difference between the velocities of the electrons and ions, and may then be developed after powers of small quantities. In the case that the ions and the electrons have a Maxwellian distribution, we get according to Braginskij [14],

$$\begin{aligned} (a) \quad m_1 n_1 \frac{dc_{10}}{dt} &= R_1 = R_{12} \approx -m_1 n_1 \frac{1}{\tau_1} u_0, \\ (b) \quad m_2 n_2 \frac{dc_{20}}{dt} &= R_2 = R_{21} \approx m_1 n_1 \frac{1}{\tau_1} u_0, \\ (c) \quad \frac{3}{2} n_1 \frac{d\Phi_1}{dt} &= Q_1 = Q_{12} \approx -Q_{21} + R_{21} \cdot u_0, \\ (d) \quad \frac{3}{2} n_2 \frac{d\Phi_2}{dt} &= Q_2 = Q_{21} \approx 3 \frac{m_1 n_1}{m_2 \tau_1} (\Phi_1 - \Phi_2). \end{aligned} \quad (2.47)$$

Here

$$\tau_1 = \tau_1^2 = \frac{3\sqrt{m}\Phi_1^{3/2}}{4\sqrt{2\pi}\lambda e_1^2 e_2^2 n_2}, \quad (2.48)$$

and we immediately see from equation (2.47a) that  $\tau_1$  is the characteristic time of change of momentum of the electrons because of collisions with the ions.

The characteristic time of change of momentum for the ions because of



collisions with electrons,  $\tau_2^1$ , is much larger (2.47b),

$$\tau_2^1 = \frac{m_2 n_2}{m_1 n_1} \tau_1^2 \quad (2.49)$$

Further, equations (c) and (d) of the set (2.47) tell us that the relaxation times for energy are

$$\tau_{12} = \frac{1}{2} \frac{m_2}{m_1} \tau_1 \quad (2.50)$$

$$\tau_{21} = \frac{1}{2} \frac{m_2 n_2}{m_1 n_1} \tau_1$$

i. e. for the same particle density,  $n_1 = n_2$ , we have

$$\tau_{12} = \tau_{21} = \frac{1}{2} \tau_2^1 = \frac{1}{2} \frac{m_2}{m_1} \tau_1^2 \quad (2.51)$$

The characteristic times  $\tau_{11}$ ,  $\tau_{22}$ ,  $\tau_1^1$  and  $\tau_2^2$  cannot be evaluated in the same, relatively simple manner because a series development of  $\left(\frac{\partial f_\alpha}{\partial t}\right)_\alpha$  after small quantities is no longer possible. To find these times we must evaluate  $R_{\alpha\alpha}$  and  $Q_{\alpha\alpha}$  in other ways with the aid of equation (2.45). Using a procedure which will not be described here, Braginskij has found even these times,

$$\tau_{11} = \frac{3 \sqrt{m_1} \phi_1^{3/2}}{4 \sqrt{\pi} e_1^4 n_1} = \sqrt{2} \tau_1 \quad (2.52)$$

$$\tau_{22} = \frac{3 \sqrt{m_2} \phi_2^{3/2}}{4 \sqrt{\pi} e_2^4 n_2} = \sqrt{2} \frac{m_2}{m_1} \tau_1$$

and moreover,

$$\tau_1^1 = \tau_{11}, \quad \tau_2^2 = \tau_{22} \quad (2.53)$$

It is worth noting that these relaxation times, derived with the aid of Landau's collision integral, agree with the times found by Spitzer [15] for the establishment of equilibrium of energy between two groups of particles with approximate Maxwellian distribution,

$$\tau_{\alpha\beta} = \frac{3 m_\alpha m_\beta}{8 \sqrt{2\pi} \lambda e_\alpha^2 e_\beta^2 n} \left( \frac{\phi_\alpha}{m_\alpha} + \frac{\phi_\beta}{m_\beta} \right)^{3/2} \quad (\alpha, \beta = 1, 2) \quad (2.54)$$

and with Chandrasekhar's [16] times  $\tau_{\alpha\beta}^{\beta}$  for the establishment of equilibrium of momentum between two groups  $\alpha$  and  $\beta$ ,

$$\tau_{\alpha}^{\beta} = \frac{3 \sqrt{3} \sqrt{m_{\alpha}} \frac{1}{2}}{8 \pi \lambda e_{\alpha}^2 e_{\beta}^2 n_{\beta}} \frac{1}{\phi\left(\sqrt{\frac{3m_{\alpha}}{2m_{\beta}}}\right) - G\left(\sqrt{\frac{3m_{\alpha}}{2m_{\beta}}}\right)} \quad (2.55)$$

Here the functions  $\phi(x)$  and  $G(x)$  are defined by

$$\phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\xi^2} d\xi, \quad G(x) = \frac{\phi(x) - x\phi^1(x)}{2x^2} \quad (2.56)$$

Spitzer's times (2.54) for  $\tau_{\alpha\beta}$  agree exactly with the times (2.50) and (2.52) if we put  $m_1 \ll m_2$ , and Chandrasekhar's times (2.56) for  $\tau_{\alpha}^{\beta}$  agree with the times (2.48), (2.49) and (2.53) on the same conditions, apart from some insignificant numerical factors.

According to the above formulas the following relations exist between the relaxation times of energy and momentum,  $\tau_{\alpha\beta}$  and  $\tau_{\alpha}^{\beta}$ , in an electron-ion gas ( $n_1 \approx n_2$ ),

$$\tau_{11} : \tau_{22} : \tau_{21} : \tau_{12} \approx 1 : \sqrt{\frac{m_2}{m_1}} : \frac{m_2}{m_1} : \frac{m_2}{m_1} \quad (2.57)$$

$$\tau_1^1 : \tau_2^2 : \tau_2^1 : \tau_1^2 \approx 1 : \sqrt{\frac{m_2}{m_1}} : \frac{m_2}{m_1} : 1$$

and moreover

$$\tau_{11} = \tau_1^1 = \sqrt{2} \tau_1 \quad (2.59)$$

The characteristic times for the establishment of equilibrium of momentum, i.e. isotropic velocity distribution, thus coincide with the times for the establishment of equilibrium of energy as concerns the interactions electrons  $\leftrightarrow$  electrons, ions  $\leftrightarrow$  ions, and electrons  $\rightarrow$  ions. But with respect to interactions ions  $\rightarrow$  electrons we see that the ions will make the distribution of the electrons isotropic in a much shorter time than they will need to equalize the temperatures. We must thus expect the electrons to acquire an isotropic velocity distribution very rapidly. For the ions, on the other hand, the two processes will develop with equal rapidity.

It might be interesting to make a comparison with the results obtained when only taking the short-range collisions into account. Chapman and Cowling give the following value for the collision time [4],

$$\tau_{\alpha}^{\beta} = \frac{\mu_{\alpha\beta}^{\frac{1}{2}}}{2 \sqrt{2\pi} \sigma_{\alpha\beta}^2 n_{\beta} \frac{1}{2}} \quad (2.59)$$

where  $\mu_{\alpha\beta}$  is the reduced mass for two particles  $\alpha$  and  $\beta$ ,

$\mu_{\alpha\beta} = \frac{m_\alpha m_\beta}{m_\alpha + m_\beta}$ , while  $\sigma_{\alpha\beta}$  is a mean impact parameter.

For  $\sigma_{\alpha\beta}$  we substitute the value that corresponds to a relative deflection  $\pi/2$ ,

$$\sigma_{\alpha\beta} \sim \frac{e_\alpha e_\beta}{\sigma_{\alpha\beta} w_{\alpha\beta}^2} \quad (2.60)$$

( $w_{\alpha\beta}$  is the relative velocity between the particles).

If we take into account that  $\mu_{11} = \frac{m_1}{2}$ ,  $\mu_{22} = \frac{m_2}{2}$  and  $\mu_{12} \approx m_1$ , ( $m_1 \ll m_2$ ), and that mean values of  $w_{\alpha\beta}$  are

$$w_{11} \sim \sqrt{2} \left( \frac{3\phi}{m_1} \right)^{\frac{1}{2}}, \quad w_{22} \sim \sqrt{2} \left( \frac{3\phi}{m_2} \right)^{\frac{1}{2}}, \quad w_{12} \sim \left( \frac{3\phi}{m_1} \right)^{\frac{1}{2}}, \quad (2.61)$$

we get for  $\tau_{\alpha c}^\beta$ ,

$$\tau_{1c}^1 = \frac{9 \sqrt{m_1} \phi^{\frac{3}{2}}}{4\pi e_1^4 n_1}, \quad \tau_{2c}^2 = \frac{9 \sqrt{m_2} \phi^{\frac{3}{2}}}{4\pi e_2^4 n_2}, \quad (2.62)$$

$$\tau_{1c}^2 = \frac{9 \sqrt{m_1} \phi^{\frac{3}{2}}}{2\sqrt{2} e_1^2 e_2^2 n_2}, \quad \tau_{2c}^1 = \frac{m_2}{m_1} \tau_{1c}^2.$$

The mutual proportions are thus the same as for long-range interactions (2.57),

$$\tau_{1c}^1 : \tau_{2c}^2 : \tau_{2c}^1 : \tau_{1c}^2 = 1 : \sqrt{\frac{m_2}{m_1}} : \frac{m_2}{m_1} : 1. \quad (2.63)$$

But we immediately see that the deflection time for short-range collisions is larger by a factor  $\sim 6\lambda$ . According to Section 4,

$$\lambda = \ln D/q_0 \approx \ln \left[ \frac{3}{2} \left( \frac{\phi^3}{\pi e^4 n} \right)^{\frac{1}{2}} \right]. \quad (2.64)$$

The quantity  $\lambda$  grows slowly with increasing temperature  $\phi$  ( $=kT$ ), and decreasing density  $n$ , and stays within the regions of temperature and density pertinent to plasma physics of the order of magnitude  $\sim 20$  [15].

The collision times for long-range interactions thus are less than the short-range collision times by a factor  $\sim 10^2$ . A grave error is therefore committed by only taking short-range collisions into account, as pointed out by Cohen et al. [17]. This is, however, permissible in the case of gases with low temperature and high density.

#### 14. INTERACTIONS WITH THE ENVIRONMENT

In Section 8 we showed that the force term  $\langle F_{\alpha} F_{\alpha m} \rangle$  of the averaged Liouville's equation (1.8) may be split into the following parts,

$$f_{\alpha} F_{\alpha 0} + f_{\alpha} \sum_{\beta} \int F_{\alpha\beta} f'_{\beta} d\mathbf{r}' d\mathbf{c}' + \sum_{\beta} \int F_{\alpha\beta} (f_{\alpha\beta} - f_{\alpha} f'_{\beta}) d\mathbf{r}' d\mathbf{c}' \quad (2.65)$$

The first part is the external macroscopic force field while the second part is defined as the internal macroscopic force field,

$$F_{\alpha} = \sum_{\beta} \int F_{\alpha\beta} f'_{\beta} d\mathbf{r}' d\mathbf{c}' \quad (2.66)$$

The electromagnetic field involved in (2.66) satisfies Maxwell's equations, as shown in Section 3. Finally, the last part of (2.65) is due to the correlations between the different kinds of particles and gives origin to the so-called collision term.

The important thing about this result is that interactions between molecular systems in the correlation region (where  $f_{\alpha\beta} - f_{\alpha} f'_{\beta} = \varphi_{\alpha\beta} \neq 0$ ) cannot be represented by macroscopic force fields.

Part of the macroscopic field  $F_{\alpha}$  is due to the external field  $F_{\alpha 0}$  and represents the effect of the environment on the system. But recalling the above statement, we cannot expect to be able to represent the total effect of the environment by macroscopic fields, dependent on time and position.

Apart from this more indirect effect, we must also take into account the possible occurrence of direct effects having the character of random collisions between gas molecules and the molecules of the environment, the mutual distance of which is less than a certain correlation length. The environment may consist of other gases, fluids or solid matter. Thus, in general, a knowledge of the detailed microscopic structure both of the system and the surroundings is absolutely necessary to give an exact description of the development of the system by equation (1.62). This really means that we extend the system to include part of the surroundings.

This, however, we do not wish to do, and we must consequently hereafter neglect direct "collisions" between system and environment and assume that the total effect of the surroundings on the system may be represented by external macroscopic force fields which depend on time and position:  $F_{\alpha 0} = F_{\alpha 0}(\mathbf{r}, t)$ . This assumption is justified if the gas is sufficiently far away from the environments or if the molecules at the surface of the gas are in local statistical equilibrium with the molecules in the nearest environment.

If the environment is constituted by another (ionized) gas, we have seen that eventually the collisions will invariably lead to the attainment of the equilibrium state. We must expect similar conditions when the surroundings consist of solid matter or fluids. (The entropy of the system can admittedly diminish because of interaction with the environment. This, however, is always accompanied by a corresponding increase in the entropy of the environment, so that the total change is positive.)

## 15. EXTERNAL TIME-DEPENDENT MAGNETIC FIELD

Before leaving the study of the statistical properties of ionized gases, we shall consider a state of affairs which at first appears paradoxical, but which actually has a natural explanation.

We have seen that the only physical effect which contributes to the change in entropy when the "entropy flow"  $(\bar{n}_\alpha \frac{d}{dt} \ln f_\alpha)$  is zero, is the so-called "entropy source density"  $\frac{dH_\alpha}{dt}$ . The latter is always negative.

As a result of molecular interactions the entropy of a system will decrease towards a lower, stable value  $(H_\alpha)$  while the state of the system, represented by  $f_\alpha$ , will simultaneously approach statistical equilibrium, i.e. isotropic Maxwell-Boltzmann distribution.

Suppose that we have an external magnetic field in the gas, and that there is present a time change of the field with such a short period  $\tau$  that the collisions are unable to "smooth out" the effect in less than the time  $\tau_r$  ( $\tau \ll \tau_r$ ). On the condition  $\frac{2\pi}{\omega} \ll \tau$  ( $\omega = \frac{eB}{mc}$ ) the magnetic moment

of a particle,  $\mu = \frac{\frac{1}{2} mc^2}{B}$ , is an adiabatic constant, and the transverse particle energy will therefore change proportionally to  $B$ , while the longitudinal one,  $\frac{1}{2} mc^2_{||}$ , is of course unchanged. Analogous conditions exist even when  $\frac{2\pi}{\omega} \ll \tau_k$  is not satisfied.

It appears as if the system retreats from statistical equilibrium because of the introduction of anisotropy. If, however, we have a look at the expression for  $\frac{dH_\alpha}{dt}$ , we find that there is no corresponding change in the entropy,

as the term  $n_\alpha \frac{d}{d\epsilon} \cdot F_\alpha \ln f_\alpha$  (2.15), representing the contribution to  $\frac{dH_\alpha}{dt}$  from external fields, disappears. The solution of this apparent paradox is immediately seen if we let the magnetic field revert to its original value. Provided that the collisions have not had the time to cause disturbance, we shall again have the original isotropic state. The process is reversible, at least as far as the system gas-magnetic field is concerned, and is consequently not accompanied by a change in entropy,  $\left( \frac{dH_\alpha}{dt} = 0 \right)$ .

A periodic change in the field with characteristic time equal to or greater than the relaxation time for the gas ( $\tau \gtrsim \tau_r$ ), however, will result in decreasing entropy, as the collisions then have the time to smooth out of the difference between the transverse and the longitudinal energy [18].

Ultimately then, only the collisions can lead to a change in entropy, but any (reversible) deviation from the isotropic Maxwell distribution in the state of the system will enable the collisions to increase the entropy of the system further.

Finally a word about the concept of "collisions". The "collision term" in Boltzmann's equation has been the source of much confusion, evidenced, for instance, by the many forms of the term. This is the more strange when one considers the fundamental importance of the so-called collisions for the statistical development of the system.

This untenable situation is clarified, however, when we take our point of departure in the exact Liouville equation and not in the Boltzmann equation with a more or less arbitrary collision term.

## 16. THE EQUILIBRIUM CONFIGURATION FOR THE SYSTEM

### 16.1 DEDUCTION FROM MICROSCOPIC THEORY

Statistical equilibrium for a system is characterized by the fulfillment of two requirements:

- (1) Internal equilibrium for the system.
- (2) Equilibrium between the system and the environment.

A macroscopic system always has an internal structure, and can consequently be subdivided into component systems, i.e. molecules, groups of molecules etc.

The requirements (1) and (2) are again valid for all macroscopic component systems in statistical equilibrium. In this case, however, the environment with respect to a single given component system includes all other component systems.

We must assume that all (component) systems have a natural tendency toward statistical equilibrium because of the intermolecular interactions in the system and with the environment. If we denote the negative entropy of the (component) system by  $H$ , we can express the irreversible tendency in the following manner,

$$\left( \frac{\partial_c H}{\partial t} \right)_{\text{sys.}} \leq 0, \quad \left( \frac{\partial_c H}{\partial t} \right)_{\text{env.}} \leq 0. \quad (2.70)$$

Both interactions within the system and with the surroundings will lead to increasing entropy. The requirements (1) and (2) can now be expressed as

$$\begin{aligned} (1) \quad & \left( \frac{\partial_c H}{\partial t} \right)_{\text{sys.}} = 0, \\ (2) \quad & \left( \frac{\partial_c H}{\partial t} \right)_{\text{env.}} = 0. \end{aligned} \quad (2.71)$$

The relations (2.70-71) are only valid for *macroscopic* component systems. For microscopic or molecular systems the so-called "principle of microscopic reversibility" is applicable, meaning that from a microscopic point of view the development is invariant with respect to inversion of time ( $t \rightarrow -t$ ). (In the case that we have an external magnetic field, its direction must be reversed ( $B \rightarrow -B$ ).) The equations of motion of the single molecules are symmetrical with respect to time.

In the preceding we have treated a composite gas partly as a system and partly as being composed of independent component systems (gases).

In the former case we defined the thermal velocities in relation to the mass velocity  $\mathbf{c}_0$  for the whole gas ( $\mathbf{C}_\alpha = \mathbf{c}_\alpha - \mathbf{c}_0$ ), while in the latter case the thermal velocities are more naturally defined in relation to the mean velocities  $\mathbf{c}_{\alpha 0}$  ( $\mathbf{C}_\alpha' = \mathbf{c}_\alpha - \mathbf{c}_{\alpha 0}$ ) of the component gases. In this case we further define average values and flux vectors of molecular quantities for each component gas in the same way as done earlier for a simple gas. We then get as many sets of such quantities as there are components in the gas, and as many sets of macroscopic transport equations.

Under the first point of view the interactions between the component gases will have the form of internal forces, the effects of which cancel when the gas is viewed as a whole. Under the latter point of view the interactions between one component gas and the other components will have the form of forces between one component and the surroundings. The requirements (1) and (2) will be satisfied in both cases if the conditions

$$\left( \frac{\partial_c H_\alpha}{\partial t} \right)_\beta = 0, \quad \left( \frac{\partial_c H_\alpha}{\partial t} \right)_{\text{env.}} = 0 \quad (2.72)$$

for all  $\alpha$  and  $\beta$ , are satisfied. The first condition means that the distributions  $f_\alpha$  have the form (2.40),

$$f_\alpha = f_\alpha^{(0)} = n_\alpha \left( \frac{m_\alpha}{2\pi\mathfrak{J}} \right)^{3/2} e^{-\frac{m_\alpha (\mathbf{c}_\alpha - \mathbf{c}_0)^2}{2\mathfrak{J}}}, \quad \alpha = 1, 2, \dots \quad (2.73)$$

The mean velocities  $\mathbf{c}_{\alpha 0}$  and the temperatures  $\mathfrak{J}_\alpha$  are the same for all component gases, i.e.  $\mathbf{c}_0$  and  $\mathfrak{J}$ . The second condition is satisfied if we disregard possible collision terms representing interaction with the environment in Boltzmann's equation. When we impose the stationary condition ( $\frac{\partial}{\partial t} = 0$ ) this equation gets the form

$$\mathbf{c}_\alpha \cdot \frac{\partial f_\alpha}{\partial \mathbf{r}} + (\mathbf{F}_\alpha + \mathbf{c}_\alpha \times \boldsymbol{\omega}_\alpha) \cdot \frac{\partial f_\alpha}{\partial \mathbf{c}_\alpha} = 0, \quad (2.74)$$

or, if we introduce the thermal velocity  $\mathbf{C}_\alpha = \mathbf{c}_\alpha - \mathbf{c}_0$  and divide by  $f_\alpha$ ,

$$\begin{aligned} \mathbf{c}_0 \cdot \frac{\partial \ln f_\alpha}{\partial \mathbf{r}} + \mathbf{C}_\alpha \cdot \frac{\partial \ln f_\alpha}{\partial \mathbf{r}} + [\mathbf{F}_\alpha - \mathbf{c}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \mathbf{c}_0 + \mathbf{c}_0 \times \boldsymbol{\omega}_\alpha] \cdot \frac{\partial \ln f_\alpha}{\partial \mathbf{C}_\alpha} + \\ + (\mathbf{C}_\alpha \times \boldsymbol{\omega}_\alpha) \cdot \frac{\partial \ln f_\alpha}{\partial \mathbf{C}_\alpha} - \frac{\partial \ln f_\alpha}{\partial \mathbf{C}_\alpha} \mathbf{C}_\alpha : \frac{\partial}{\partial \mathbf{r}} \mathbf{c}_0 = 0. \end{aligned} \quad (2.75)$$

In contrast to earlier convention  $\mathbf{F}_\alpha$  does now not include the magnetic force  $\mathbf{c}_\alpha \times \boldsymbol{\omega}_\alpha$ ,  $\boldsymbol{\omega}_\alpha = \frac{e_\alpha \mathbf{B}}{m_\alpha c}$ .

From this equation we can now derive the equilibrium conditions for the macroscopic quantities  $n_\alpha$ ,  $\mathbf{c}_0$ ,  $\mathfrak{J}$ ,  $\mathbf{F}_\alpha$  and  $\boldsymbol{\omega}_\alpha$ .

In equation (2.75) we substitute the expressions obtained for  $\frac{\partial \ln f_\alpha}{\partial r}$  and  $\frac{\partial \ln f_\alpha}{\partial C_\alpha}$  from equation (2.73), getting

$$\begin{aligned} c_0 \cdot \frac{\partial \ln n_\alpha / \mathfrak{f}^{3/2}}{\partial r} + C_\alpha \cdot \left[ \frac{\partial \ln n_\alpha / \mathfrak{f}^{3/2}}{\partial r} - \frac{m_\alpha}{\mathfrak{f}} (F_\alpha + c_0 \times \omega_\alpha - c_0 \cdot \frac{\partial}{\partial r} c_0) \right] + \\ + \left[ C_\alpha^2 \frac{1}{2} c_0 \cdot \frac{\partial \ln \mathfrak{f}}{\partial r} + C_\alpha C_\alpha : \frac{\partial}{\partial r} c_0 \right] \frac{m_\alpha}{\mathfrak{f}} + C_\alpha^2 C_\alpha \cdot \frac{m_\alpha}{2 \mathfrak{f}} \frac{\partial \ln \mathfrak{f}}{\partial r} = 0. \end{aligned} \quad (2.76)$$

This is an identity in  $C_\alpha$ , and the coefficients of the powers of the third, second, first and zero degree must therefore be zero. This gives the equations (2.77), (2.78), (2.80) and (2.85).

We get, to start with,

$$C_\alpha^2 C_\alpha \cdot \frac{\partial \ln \mathfrak{f}}{\partial r} = 0 \quad \text{i.e.} \quad \frac{\partial \ln \mathfrak{f}}{\partial r} = 0 \quad \text{i.e.} \quad \mathfrak{f} = \text{Const.} \quad (2.77)$$

Further, using (2.77),

$$C_\alpha C_\alpha : \frac{\partial}{\partial r} c_0 = 0 \quad \text{i.e.} \quad \frac{1}{2} \left( \frac{\partial}{\partial r} c_0 + \frac{\partial^\sim}{\partial r} c_0 \right) = e = 0. \quad (2.78)$$

The *deformation tensor*  $e$  is thus zero, and the gas consequently moves in a screw motion like a rigid body,

$$c_0 = u + \omega \times r, \quad u \parallel \omega, \quad (2.79)$$

where  $u$  and  $\omega$  are constants.

We further derive from equation (2.76)

$$C_\alpha \cdot \left[ \frac{\partial \ln n_\alpha}{\partial r} - \frac{m_\alpha}{\mathfrak{f}} (F_\alpha + c_0 \times \omega_\alpha - c_0 \cdot \frac{\partial}{\partial r} c_0) \right] = 0, \quad (2.80)$$

or

$$\frac{\partial \ln n_\alpha}{\partial r} = \frac{m_\alpha}{\mathfrak{f}} (F_\alpha + c_0 \times \omega_\alpha - c_0 \cdot \frac{\partial}{\partial r} c_0).$$

As  $c_0$  has the form (2.79), the term  $c_0 \cdot \frac{\partial}{\partial r} c_0$  may be transformed into  $\omega \times c_0$  and equation (2.80) can be written

$$\frac{\partial \ln n_\alpha}{\partial r} = \frac{m_\alpha}{\mathfrak{f}} (F_\alpha + c_0 \times \Omega_\alpha), \quad \Omega_\alpha = \omega_\alpha + \omega. \quad (2.81)$$

Now,

$$c_0 \times \omega = (\omega \times r) \times \omega = \omega^2 r - (\omega \cdot r) \omega = \omega^2 r_\perp, \quad (2.82)$$



where  $r_{\perp}$  is the component of  $r$  normal to the axis of the screw motion (2.79). We can therefore write  $c_o \times \omega$  as the gradient of a centrifugal potential  $\phi_c$ ,

$$c_o \times \omega = - \frac{d\phi_c}{dr}, \quad \phi_c = - \frac{1}{2} \omega^2 r_{\perp}^2. \quad (2.83)$$

Substitution in equation (2.81) shows that it must be possible to derive the vector  $F_{\alpha} + c_o \times \omega_{\alpha}$  from the potential  $\phi_{\alpha}$ ,

$$F_{\alpha} + c_o \times \omega_{\alpha} = - \frac{d\phi_{\alpha}}{dr}, \quad \phi_{\alpha} = - \frac{\beta}{m_{\alpha}} \ln n_{\alpha} - \phi_c. \quad (2.84)$$

Therefore,

$$n_{\alpha} = n_{\alpha 0} e^{-\frac{m_{\alpha}}{\beta} (\phi_{\alpha} + \phi_c)}, \quad n_{\alpha 0} = \text{const.} \quad (2.85)$$

The last relation obtained from equation (2.76),

$$c_o \cdot \frac{d \ln n_{\alpha}}{dr} = 0 \quad \text{or} \quad c_o \cdot F_{\alpha} = -c_o \cdot \frac{d\phi_{\alpha}}{dr} = 0, \quad (2.86)$$

means that the force  $F_{\alpha}$  must everywhere be normal to the velocity  $c_o$ , so that no work is done and the field is "force-free". The velocity  $c_o$  must lie along an equi-potential surface  $\phi_{\alpha} = \text{Const.}$

In the case of a pure translational motion  $c_o = u$ , the potential is thus cylindrical,  $\phi_{\alpha} = \phi_{\alpha}(r, \beta)$ , with the cylinder axis (z-axis) along  $u$ , while for a rotational motion  $c_o = \omega \times r$  the potential is rotationally symmetrical with  $\omega$  as the axis of rotation:  $\phi_{\alpha} = \phi_{\alpha}(r, z)$ . If both  $u$  and  $\omega \neq 0$ , then  $\phi_{\alpha}$  is constant along helical trajectories with  $u$  ( $\parallel \omega$ ) as the axis.

The contribution to  $F_{\alpha}$  from an electric field  $E$  is  $\epsilon_{\alpha} = \frac{e_{\alpha}}{m_{\alpha}} E$ .

If  $G_{\alpha}$  denotes the rest of  $F_{\alpha}$  (gravitational fields, etc.) we have,

$$F_{\alpha} = \epsilon_{\alpha} + G_{\alpha}. \quad (2.87)$$

Provided that  $G_{\alpha}$  may be derived from a potential

$$G_{\alpha} = - \frac{d\phi_{\alpha G}}{dr}, \quad (2.88)$$

equation (2.84) gives

$$\epsilon_{\alpha} + c_o \times \omega_{\alpha} = - \frac{d}{dr} (\phi_{\alpha} - \phi_{\alpha G}), \quad (2.89)$$

meaning that the vector is vorticity-free, or, as

$$\mathbf{e}_\alpha = \frac{e_\alpha}{m_\alpha} \mathbf{E} \quad \text{and} \quad \boldsymbol{\omega}_\alpha = \frac{1}{c} \frac{e_\alpha}{m_\alpha} \mathbf{B} ,$$

we have

$$\frac{d}{dr} \times (\mathbf{E} + \frac{1}{c} \mathbf{e}_0 \times \mathbf{B}) = 0 . \quad (2.90)$$

But this condition means that the magnetic flux through a surface that follows the motion of the gas will be constant during the motion [15], and the magnetic field will consequently be "frozen into" the gas when the latter is in statistical equilibrium.

According to the above, the assumed tendency of the field to remain frozen in [15] is a consequence of the natural tendency of the system towards equilibrium (Section 12).

The equations (2.77), (2.79), (2.85) and (2.86) as well as the two additional conditions that the temperature and the mean velocity be the same for all component gases  $\alpha$ , express the characteristic conditions of a gas in statistical equilibrium,

$$\mathcal{J} = \text{Const.}, \quad \mathbf{e}_0 = \mathbf{u} + \boldsymbol{\omega} \times \mathbf{r}, \quad n_\alpha = n_{\alpha 0} e^{-\frac{m_\alpha}{\mathcal{J}} (\phi_\alpha + \phi_c)}, \quad (2.91)$$

$$\mathbf{e}_0 \cdot \frac{d\phi_\alpha}{dr} = 0, \quad \mathcal{J}_\alpha = \mathcal{J}, \quad \mathbf{e}_{\alpha 0} = \mathbf{e}_0 .$$

The three first equations may be expressed on differential form

$$\frac{d \ln \mathcal{J}}{dr} = 0, \quad \mathbf{e} = 0, \quad \frac{d\mu_\alpha}{dr} = 0, \quad (2.92)$$

when  $\frac{d\mu_\alpha}{dr}$  is defined by

$$\frac{d\mu_\alpha}{dr} = \frac{\ln n_\alpha}{dr} - \frac{m_\alpha}{\mathcal{J}} (\mathcal{F}_\alpha + \mathbf{e}_0 \times \boldsymbol{\Omega}_\alpha), \quad \boldsymbol{\Omega}_\alpha = \boldsymbol{\omega}_\alpha + \boldsymbol{\omega}. \quad (2.93)$$

In an arbitrary state these three quantities constitute a measure of the deviation from statistical equilibrium. In that case  $\mathbf{e}_0 \times \boldsymbol{\omega}$  must be replaced by  $-\mathbf{e}_0 \cdot \frac{d}{dr} \mathbf{e}_0$ .

It follows from the set (2.91) that  $\mathbf{j}^* = 0$  (equation (1.47)), and the current density is then equal to the convective flow  $q_e \mathbf{e}_0$ . Maxwell's equations therefore assume the form ( $\frac{d}{dt} = 0$ ),

$$\frac{d}{dr} \cdot \mathbf{E} = 4\pi q_e, \quad \frac{d}{dr} \cdot \mathbf{B} = 0, \quad (2.94)$$

$$\frac{d}{dr} \times \mathbf{E} = 0, \quad \frac{d}{dr} \times \mathbf{B} = \frac{4\pi}{c} q_e \mathbf{e}_0 .$$

This set of equations, together with equations (2.80), (2.85) and (2.79),

$$\mathbf{E} + \frac{1}{c} \mathbf{c}_0 \times \mathbf{B} = - \frac{\partial \phi}{\partial \mathbf{r}}, \quad (\phi = \frac{m_\alpha}{e_\alpha} \phi_\alpha), \quad (2.95)$$

$$\mathbf{E} \cdot \mathbf{c}_0 = 0, \quad \mathbf{c}_0 = \mathbf{u} + \boldsymbol{\omega} \times \mathbf{r}, \quad q_e = \sum_\alpha e_\alpha n_\alpha,$$

gives the field configurations that are characteristic of statistical equilibrium. We must assume that the fields possess a natural tendency towards this equilibrium configuration.

We have here assumed that the only forces are electric or magnetic ones ( $G_\alpha = 0$ ).

The solution of the equations (2.94) are, when disregarding border effects,

$$\mathbf{E} = - \frac{\partial}{\partial \mathbf{r}} \phi_e + \mathbf{E}_0, \quad \mathbf{B} = \frac{\partial}{\partial \mathbf{r}} \times \mathbf{A} + \mathbf{B}_0, \quad (2.96)$$

$$\phi_e(\mathbf{r}) = \int \frac{q'_e d\tau'}{|\mathbf{r} - \mathbf{r}'|}, \quad \mathbf{A} = \int \frac{1}{c} \frac{q'_e \mathbf{c}'_0 d\tau'}{|\mathbf{r} - \mathbf{r}'|}.$$

Here  $\mathbf{E}_0$  and  $\mathbf{B}_0$  are the external fields that satisfy the homogeneous Maxwell equations.

In the special case that  $\mathbf{c}_0 = \text{Const.} = \mathbf{u}$  we derive the following relation for the internal fields (exclusive of  $\mathbf{E}_0$  and  $\mathbf{B}_0$ ) from equations (2.96),

$$\mathbf{B} = \frac{1}{c} \mathbf{E} \times \mathbf{c}_0. \quad (2.97)$$

Non-relativistically, the internal magnetic field must therefore be zero, and in this case the external magnetic field is frozen in the gas.

In the case of a rotating gas the conditions become more complex. The relation (2.97), for instance, is no longer valid.

The above equilibrium conditions (2.91) and (2.92) are microscopically founded and rest on the validity of the H-theorem. In classical thermodynamics the equilibrium conditions are derived by macroscopic arguments that have the character of postulates. It might be interesting to see how the usual postulates must be modified to be consistent with the results of microscopic theory.

## 16.2 COMPARISON WITH MACROSCOPIC THEORY

The thermodynamical expression for the entropy (per unit volume) for an ideal gas ( $nD^3 \gg 1$ ) is [4].

$$S_\alpha = - n_\alpha k (\ln n_\alpha + \frac{3}{2} \ln \frac{m_\alpha}{2\pi kT} - \frac{3}{2}), \quad (2.98)$$

while the enthalpy  $W_\alpha$  is given by

$$W_{\alpha} = \frac{5}{2} n_{\alpha} k T . \quad (2.99)$$

The thermodynamic or Gibbs potential  $G_{\alpha} = W_{\alpha} - S_{\alpha} T$  is consequently given by ( $\beta = kT$ ).

$$G_{\alpha} = n_{\alpha} \beta \left( \ln n_{\alpha} + \frac{3}{2} \ln \frac{m_{\alpha}}{2 \pi \beta} + 1 \right) . \quad (2.100)$$

Further, the chemical potential  $\mu_{\alpha}^0$  is defined as thermodynamic potential per molecule,

$$\mu_{\alpha}^0 = G_{\alpha} / n_{\alpha} = \beta \left( \ln n_{\alpha} + \frac{3}{2} \ln \frac{m_{\alpha}}{2 \pi \beta} + 1 \right) . \quad (2.101)$$

In the case that we have external and internal fields of force  $F_{\alpha}$  that may be derived from a potential  $m_{\alpha} \phi_{\alpha}$  the expression (2.101) must be replaced by

$$\mu_{\alpha} = \mu_{\alpha}^0 + m_{\alpha} \phi_{\alpha} . \quad (2.102)$$

The conditions that are usually assumed for thermodynamic equilibrium are constant temperature, velocity and chemical potential,

$$\beta = \text{Const.}, \quad c_0 = u, \quad \mu_{\alpha} = \text{Const.} \quad (2.103)$$

These three conditions may be written on differential form,

$$\frac{\partial \ln \beta}{\partial r} = 0, \quad \frac{\partial}{\partial r} c_0 = 0, \quad \frac{\partial \mu_{\alpha}}{\partial r} = 0, \quad (2.104)$$

where

$$\frac{\partial \mu_{\alpha}}{\partial r} = \beta \frac{\partial \ln n_{\alpha}}{\partial r} - m_{\alpha} F_{\alpha} . \quad (2.105)$$

These are the conditions assumed by for instance H. S. Green [8]. He further assumes arbitrarily that the relation

$$B = \frac{1}{c} E \times c_0 \quad (2.106)$$

is valid in equilibrium between the internal fields. Non-relativistically we then have  $B = 0$ .

The conditions (2.103) or (2.104) and (2.106), which must be considered as arbitrary macroscopic postulates, in the case of no rotation ( $\omega = 0$ ) and no magnetic field ( $\mathbf{e}_0 = 0$ ), then are quite equivalent with the three first conditions (2.91) or (2.92) which are founded on microscopic theory. By the latter procedure we get in addition the three last of the conditions (2.91), which cannot be macroscopically proved.

Consider the case that the body has a constant rotation  $\omega$ . If we then add the centrifugal potential  $m_{\alpha} \phi_c = -\frac{1}{2} m_{\alpha} \omega^2 r^2$  to the chemical potential (2.102),

$$\mu_{\alpha} = \mu_{\alpha}^0 + m_{\alpha} \phi_{\alpha} - \frac{1}{2} m_{\alpha} \omega^2 r^2, \quad (2.107)$$

and further require that the magnetic force  $\mathbf{c}_0 \times \mathbf{u}_{\alpha}$  can be derived from a potential which may be included in  $\phi_{\alpha}$ , i.e.

$$\frac{d}{dt} \times (\mathbf{c}_0 \times \mathbf{B}) = 0 \quad (2.108)$$

( $\mathbf{B}$  is the sum of the internal and external fields), we obtain equilibrium conditions that are quite equivalent with the conditions (2.91) or (2.92). The three last conditions (2.91) must, however, be separately postulated,

$$\mathbf{c}_0 \cdot \mathbf{F}_{\alpha} = 0, \quad \mathcal{J}_{\alpha} = \mathcal{J}, \quad \mathbf{c}_{\alpha 0} = \mathbf{c}_0. \quad (2.109)$$

We have seen that the conditions (2.91) and (2.92) are sufficient to secure that the entropy production is zero and that the state is stationary. We shall therefore use these conditions as definitions of thermodynamic or statistical equilibrium. We must, however, be aware of the apparent absence of a general agreement as to which equilibrium conditions are the correct ones.

The first part of this section is essentially a generalization of the results of Chapman and Cowling for simple gases without electromagnetic fields [4] to the electromagnetic case for composite gases.

## PART III. PHENOMENOLOGICAL THEORY OF TRANSPORT PHENOMENA

### 17. TRANSPORT PHENOMENA

The denotation "transport phenomenon" is applied to certain phenomena occurring in a gas which is not in statistical equilibrium. We have seen that any deviation from equilibrium will set off microscopic equalization processes, which, in accordance with Le Chatelier's principle, seek to counteract their cause and lead the system back to the equilibrium state. The macroscopic counterpart of the microscopic equalization tendencies are the so-called transport phenomena. The fact that a system is not in statistical equilibrium can always be traced back to disturbing interaction with the environment, with the result that the equilibrium conditions (2.91) can no longer be satisfied. (We then disregard possible changes in the internal structure of the molecules.) These disturbances set up gradients (possibly time variant) in temperature, velocity and density, that do not agree with (2.92). For composite gases the equilibrium between the component gases will moreover be destroyed. We thus get phenomena like diffusion, electric current, transport of momentum and heat conduction.

The microscopic explanation of this is that the molecules, during their disorganized thermal motion, will "transport" their molecular properties (e.g. number, electric charge, momentum and energy) from place to place. In statistical equilibrium this transport is completely random, so that the microscopic mean values disappear. Deviation from equilibrium, on the other hand, means that this is no longer the case.

Let  $\phi = \phi(r, C, t)$  denote the molecular property as before. Then

$$n\bar{\phi} = \sum_{\alpha} n_{\alpha} \bar{\phi}_{\alpha} = \sum_{\alpha} \int \phi_{\alpha} f_{\alpha} dC_{\alpha} \quad (3.1)$$

is the corresponding macroscopic property. The transport of this property is given by the so-called flux vector

$$n\bar{\phi C} = \sum_{\alpha} n_{\alpha} \overline{\phi_{\alpha} C_{\alpha}} = \sum_{\alpha} \int \phi_{\alpha} C_{\alpha} f_{\alpha} dC_{\alpha} \quad (3.2)$$

which gives the flux of the property  $\phi$  through a surface which follows the mean motion of the gas.

#### 17.1 DIFFUSION OR NUMBER TRANSPORT

If we assign to  $\phi$  the molecular property "number", i.e.  $\phi = 1$ , we get from (3.1),

$$n_{\alpha} \bar{C}_{\alpha} = \int C_{\alpha} f_{\alpha} dC_{\alpha} \quad (3.3)$$

This vector gives the number flux of molecules  $\alpha$  in relation to the mean motion of the gas. Another name for  $\bar{C}_{\alpha}$  is the "diffusion velocity" of the molecules  $\alpha$ . If we have two component gases ( $\alpha = 1$  and 2), we are usually interested in the relative diffusion velocity,

$$\begin{aligned}\bar{\mathbf{c}}_1 - \bar{\mathbf{c}}_2 &= \frac{1}{n_1} \int \mathbf{c}_1 f_1 d\mathbf{c}_1 - \frac{1}{n_2} \int \mathbf{c}_2 f_2 d\mathbf{c}_2 = \\ &= \bar{\mathbf{c}}_1 - \bar{\mathbf{c}}_2 = \mathbf{c}_{10} - \mathbf{c}_{20} = \mathbf{u}_0 ,\end{aligned}\quad (3.4)$$

which equals the difference between the mean motions of the two gases.

We have a special case when the molecules of the gases 1 and 2 are identical. The vector  $\bar{\mathbf{c}}_2 - \bar{\mathbf{c}}_1$  then gives the "self-diffusion" of the molecules, i.e. the relative diffusion of two different groups of identical molecules.

The diffusion is evidently zero when the gas is in statistical equilibrium (Eq. (2.73)),  $n_\alpha \bar{\mathbf{c}}_\alpha^{(0)} = 0$ . The symbol  $^{(0)}$  denotes statistical equilibrium.

## 17.2 ELECTRIC CHARGE TRANSPORT

The total electric current density is given by

$$\mathbf{j} = \sum_\alpha n_\alpha e_\alpha \bar{\mathbf{c}}_\alpha = \left( \sum_\alpha n_\alpha e_\alpha \right) \mathbf{c}_0 + \sum_\alpha n_\alpha e_\alpha \bar{\mathbf{c}}_\alpha , \quad (3.5)$$

and is the sum of the "convection current"  $\left( \sum_\alpha n_\alpha e_\alpha \right) \mathbf{c}_0$  and the other term

which gives the proper conduction current  $\mathbf{j}^*$ . The convection current is zero when the gas is electrically neutral.

The flux vector for electric charge is obtained from equation (3.2) by putting  $\Phi = e$ ,

$$ne\bar{\mathbf{C}} = \sum_\alpha n_\alpha e_\alpha \overline{\mathbf{C}_\alpha} = \sum_\alpha \int e_\alpha \mathbf{C}_\alpha f_\alpha d\mathbf{C}_\alpha . \quad (3.6)$$

This is identical to the conduction current  $\mathbf{j}^*$ ,

$$\mathbf{j}^* = ne\bar{\mathbf{C}} = \sum_\alpha n_\alpha e_\alpha \overline{\mathbf{C}_\alpha} = \sum_\alpha \mathbf{j}_\alpha^* . \quad (3.7)$$

The contribution to this from the molecules  $\alpha$ , i.e.  $\mathbf{j}_\alpha^* = n_\alpha e_\alpha \bar{\mathbf{c}}_\alpha$ , thus is proportional to the diffusion vector  $n_\alpha \bar{\mathbf{c}}_\alpha$ .

For a binary gas mixture we get from equation (3.7) and the relation  $\sum_\alpha n_\alpha m_\alpha \bar{\mathbf{C}}_\alpha = 0$ ,

$$\mathbf{j}^* = \frac{n_1 n_2 (m_2 e_1 - m_1 e_2)}{q} (\bar{\mathbf{c}}_1 - \bar{\mathbf{c}}_2) . \quad (3.8)$$

In this case the electric flux vector is proportional to the relative diffusion velocity. If in a plasma we denote the electrons by index 1 and the ions by index 2, i.e.  $m_1/m_2 \ll 1$ , equation (3.8) will give approximately,

$$\mathbf{j}^* = n_1 e_1 (\bar{\mathbf{c}}_1 - \bar{\mathbf{c}}_2) . \quad (3.9)$$

The current density is zero in statistical equilibrium, (Eq. (2.73)),  
 $j^{(0)} = 0$ .

### 17.3 TRANSPORT OF MOMENTUM

We have previously shown (Section 6) that the flux tensor for momentum, or the stress tensor, is found by putting  $\phi = mC$  in equation (3.2). We then get,

$$\mathbf{P} = \overline{nmCC} = \sum_{\alpha} n_{\alpha} \overline{m_{\alpha} C_{\alpha} C_{\alpha}} = \sum_{\alpha} \mathbf{P}_{\alpha} . \quad (3.10)$$

The expression can be transformed by introducing the total velocity  $c_{\alpha} = c_0 + C_{\alpha}$ ,

$$\mathbf{P} = \sum_{\alpha} n_{\alpha} \overline{m_{\alpha} c_{\alpha} c_{\alpha}} + q c_0 c_0 . \quad (3.11)$$

In statistical equilibrium, where the distribution is given by (2.73), we easily find for  $\mathbf{P}$ ,

$$\mathbf{P}^{(0)} = p \mathbf{I} , \quad p = \sum_{\alpha} n_{\alpha} \mathfrak{J}_{\alpha} = n \mathfrak{J} = nkT , \quad (3.12)$$

as  $\mathfrak{J}_{\alpha} = \mathfrak{J}$ . All shear forces disappear, and the stress tensor represents a purely hydrostatic pressure. According to equation (1.54) this can also be expressed by the condition

$$\mathbf{P}^{(0)} = \mathbf{P}^{(0)} - p \mathbf{I} = 0 . \quad (3.13)$$

### 17.4 HEAT TRANSPORT

We have earlier found that the energy flux vector is obtained by substitution of  $\phi = E = \frac{1}{2} mC^2$  in equation (3.2). The result is

$$\mathbf{q} = \overline{n \frac{1}{2} m C^2 C} = \sum_{\alpha} n_{\alpha} \overline{\frac{1}{2} m_{\alpha} C_{\alpha}^2 C_{\alpha}} = \sum_{\alpha} \mathbf{q}_{\alpha} . \quad (3.14)$$

The heat flow, as well as the diffusion, conduction current and shear forces, disappear when  $f_{\alpha}$  is isotropic in the velocity  $C_{\alpha}$ . This is especially the case for Maxwell-Boltzmann distribution (2.73) in statistical equilibrium, i.e.  $q^{(0)} = 0$ .

## 18. THE TRANSPORT EQUATIONS

In Section 7 we derived the macroscopic transport equation for the quantity  $\bar{\phi}$  where  $\phi$  is a molecular property (equation (1.57)). Three molecular properties are of special interest. They are the so-called summational invariants

$$\phi = 1 , \quad \phi = mC , \quad \phi = \frac{1}{2} mC^2 , \quad (3.15)$$



that is to say molecular number, momentum and energy. The reason that these three quantities are in a class by themselves is that the total amount of these properties is conserved during collisions between molecules,

$$n \frac{d_c \bar{\phi}}{dt} = \sum_{\alpha} n_{\alpha} \frac{d_c \bar{\phi}_{\alpha}}{dt} = \sum_{\alpha} \int \phi_{\alpha} \frac{d_c f_{\alpha}}{dt} dC_{\alpha} = 0. \quad (3.16)$$

One may satisfy oneself that equation (3.16) is correct, when  $\frac{d_c f_{\alpha}}{dt}$  is Landau's collision term, by a direct computation which is given in the Appendix. Equation (3.16) is also valid for the familiar two-particle collision integral (1.26).

The quantities (3.15) are the only ones having this property.

For a simple gas the transport equations take the form

$$\begin{aligned} (a) \quad \frac{dn}{dt} + n \frac{d}{dr} \cdot c_0 &= 0, \\ (b) \quad q \frac{d c_0}{dt} - q \bar{F} + \frac{d}{dr} \cdot p &= 0, \\ \frac{dU}{dt} + U \frac{d}{dr} \cdot c_0 + \frac{d}{dr} \cdot q - q \bar{C} \cdot F + p : \frac{d}{dr} c_0 &= 0, \end{aligned} \quad (3.17)$$

where  $U = n \frac{1}{2} m \overline{C^2} = \frac{3}{2} n \bar{\epsilon}$  is the average molecular energy, and  $p$  and  $q$  are the stress tensor (3.10) and heat flow (3.14), respectively. These three equations thus express the conservation of molecular number, momentum and energy in the gas.

For a gas with several components ( $\alpha = 1, 2, \dots$ ) we obtain similar sets for the components,

$$\begin{aligned} (a) \quad \frac{dn_{\alpha}}{dt} + n_{\alpha} \frac{d}{dr} \cdot c_0 + \frac{d}{dr} \cdot (n_{\alpha} \bar{C}_{\alpha}) &= n_{\alpha} \frac{d_c l}{dt} = 0, \\ (b) \quad \frac{d q_{\alpha} \bar{C}_{\alpha}}{dt} + q_{\alpha} \bar{C}_{\alpha} \frac{d}{dr} \cdot c_0 + \frac{d}{dr} \cdot p_{\alpha} - q_{\alpha} (\bar{F}_{\alpha} - \frac{d c_0}{dt}) + q_{\alpha} \bar{C}_{\alpha} \cdot \frac{d}{dr} c_0 &= \\ &= n_{\alpha} \frac{d_c m_{\alpha} \bar{C}_{\alpha}}{dt}, \\ (c) \quad \frac{dU_{\alpha}}{dt} + U_{\alpha} \frac{d}{dr} \cdot c_0 + \frac{d}{dr} \cdot q_{\alpha} - q_{\alpha} \bar{C}_{\alpha} \cdot (\bar{F}_{\alpha} - \frac{d c_0}{dt}) + & \\ + p_{\alpha} : \frac{d}{dr} c_0 &= n_{\alpha} \frac{d_c \frac{1}{2} m_{\alpha} \overline{C_{\alpha}^2}}{dt}, \end{aligned} \quad (3.18)$$

By adding the corresponding equations for all component gases and using equation (3.16) and the relation  $\sum_{\alpha} q_{\alpha} \bar{C}_{\alpha} = 0$  we derive,

$$\begin{aligned}
 (a) \quad & \frac{dq}{dt} + \frac{d}{dr} \cdot c_o = 0, \\
 (b) \quad & q \frac{dc_o}{dt} + \frac{d}{dr} \cdot p - \sum_{\alpha} q_{\alpha} \bar{F}_{\alpha} = 0, \quad (3.19) \\
 (c) \quad & \frac{dU}{dt} + U \frac{d}{dr} \cdot c_o + \frac{d}{dr} \cdot q - \sum_{\alpha} q_{\alpha} \overline{C_{\alpha} \cdot F_{\alpha}} + p_{\alpha} : \frac{d}{dr} c_o = 0.
 \end{aligned}$$

Here  $U = \sum_{\alpha} U_{\alpha} = \frac{3}{2} n \bar{\epsilon}$ ,  $p = \sum_{\alpha} p_{\alpha}$  and  $q = \sum_{\alpha} q_{\alpha}$  are the average molecular energy per unit volume, the stress tensor and the heat flow for the whole gas, respectively.

In the case that only electric and magnetic force fields are present,

$F_{\alpha} = \frac{e_{\alpha}}{m_{\alpha}} (E + \frac{1}{c} c_{\alpha} \times B)$ , the equation (3.19) can be further transformed,

$$\begin{aligned}
 (a) \quad & \frac{dq}{dt} + q \frac{d}{dr} \cdot c_o = 0, \\
 (b) \quad & q \frac{dc_o}{dt} - q_e (E + \frac{1}{c} c_o \times B) - \frac{1}{c} j^* \times B + \frac{d}{dr} \cdot p = 0, \quad (3.20) \\
 (c) \quad & \frac{dU}{dt} + U \frac{d}{dr} \cdot c_o + \frac{d}{dr} \cdot q - j^* \cdot (E + \frac{1}{c} c_o \times B) + p : \frac{d}{dr} c_o = 0.
 \end{aligned}$$

Here  $q_e = \sum n_{\alpha} e_{\alpha} = \sum q_{e\alpha}$  and  $j^* = \sum n_{\alpha} e_{\alpha} \bar{C}_{\alpha} = \sum j_{\alpha}^*$ , the total electric charge density and conduction current, are the sums of the partial contributions  $q_{e\alpha}$  and  $j_{\alpha}^*$ .

If we multiply equation (3.18b) by  $e_{\alpha}/m_{\alpha}$  and sum over all the following equation emerges,

$$\begin{aligned}
 & \frac{dj^*}{dt} + j^* \cdot \frac{d}{dr} \cdot c_o + \frac{d}{dr} \cdot \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}} p_{\alpha} - \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}} q_{e\alpha} (E + \frac{1}{c} c_o \times B) - \\
 & - \frac{1}{c} \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}} j_{\alpha}^* \times B + q_e \frac{dc_o}{dt} + j^* \cdot \frac{d}{dr} c_o = \sum_{\alpha} \frac{dc_j^*}{dt} \quad (3.21)
 \end{aligned}$$

Spitzer and others [15] have interpreted the latter equation as a generalized Ohm's law. In so doing they have assumed that the collision contribution is proportional to the current density  $j^*$  when the state is not appreciably different from the state of equilibrium, i.e.

$$- \sum_{\alpha} \frac{dc_j^*}{dt} = \left( \sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}} q_{e\alpha} \right) j^* / \sigma, \quad (3.22)$$

where  $\sigma$  is the electric conductivity. In the case that we neglect time

variations, quadratic terms in  $c_o$ ,  $j^*$  and their gradients, pressure gradients and the term  $j_\alpha^* \times B$ , equation (3.21) reduces to the familiar Ohm's law,

$$j^* = \sigma \left( E + \frac{1}{c} c_o \times B \right) = \sigma E^* . \quad (3.23)$$

The asterisks denote field quantities that refer to a coordinate system moving with the velocity  $c_o$ .

H. S. Green [8] has asserted that the assumption (3.22) is incorrect except in the special case that all temperature gradients are zero, and has proposed another generalization of Ohm's law. The situation is, however, far from clarified, and we shall return to it in Section 19.

Equations (3.18) and the other equations in this section that are derived from them, must be supplemented with Maxwell's electromagnetic equations (Section 3) and other pertinent equations. But it is easily verified that these equations do not constitute a complete, solvable set.

In the electromagnetic case the unknown quantities are, according to (3.28),  $(\alpha' = 1, 2, \dots, \kappa)$ ,

$$n_\alpha, c_o, U_\alpha, E, B, n_\alpha \bar{C}_\alpha, P_\alpha, q_\alpha, \frac{d_c}{dt} q_\alpha \bar{C}_\alpha, \frac{d_c}{dt} U_\alpha . \quad (3.24)$$

The number of scalar quantities thus is  $18\kappa + 9$ . But the number of equations to determine the unknowns, i.e. equations (3.28), Maxwell's equations (Section 3), the relations (3.26) and the relation  $\sum_\alpha q_\alpha \bar{C}_\alpha = 0$ , as well as the equation of state

$$\frac{1}{2} (P_\alpha)_{ii} = U_\alpha = \frac{3}{2} n_\alpha \bar{\Phi}_\alpha \quad \text{or} \quad P_\alpha = \frac{1}{3} (p)_{ii} = n_\alpha \bar{\Phi}_\alpha , \quad (3.24')$$

a total number of  $6\kappa + 15$ , are, for all  $\kappa \geq 1$ , less than the number of unknowns, and we need at least  $12\kappa - 6$  new equations for a complete, solvable set of equations.

Equation (3.24') follows directly from the definitions of the respective quantities. We can only expect it to give the real pressure for ideal gases. For real gases there is an additional term arising from the interaction of the particles [19]. We have actually confined ourselves to consider ideal gases, in imposing the assumption  $nD^3 \gg 1$  in Section 8.

It serves no purpose to derive new equations from the transport equation (1.57) by substituting for  $\phi$  new molecular properties that depend on higher powers of the velocity. This method breaks down because increasingly higher moments of the distribution function and new collision contributions  $n_\alpha \frac{d_c \bar{\Phi}_\alpha}{dt}$  are successively introduced into the set in numbers exceeding the number of new equations.

## 19. THE PHENOMENOLOGICAL RELATIONS. OHM'S LAW

The transport phenomena arise when the gas recedes from statistical equilibrium as a result of disturbing interaction with the environment. If this interaction is of a transient nature, the transport phenomena will be transient. They will die away after a time equal to the natural relaxation time of the system  $\tau_r$ . If the disturbances are constant (time independent), a stationary state will be established different from the equilibrium state, with transport phenomena that are independent of time. In general, conditions will vary with time.

The disturbances may be represented by the deviations in the temperature, velocity field, density and force field from the conditions that are characteristic of a gas in equilibrium (equations (2.91) and (2.92)). These deviations are the following,

$$\frac{\partial \mu_\alpha}{\partial \mathbf{r}}, \quad \mathbf{e}, \quad \frac{\partial \ln \mathfrak{J}}{\partial \mathbf{r}} \quad (\alpha = 1, 2, \dots), \quad (3.25)$$

where (Section 16)

$$\frac{\partial \mu_\alpha}{\partial \mathbf{r}} = \frac{\partial \ln n_\alpha}{\partial \mathbf{r}} - \frac{m_\alpha}{\mathfrak{J}} (\mathbf{F}_\alpha + \mathbf{c}_0 \times \boldsymbol{\Omega}_\alpha), \quad \boldsymbol{\Omega}_\alpha = \boldsymbol{\omega}_\alpha + \boldsymbol{\omega}. \quad (3.26)$$

Like the transport vectors, the above three quantities are all zero in the state of equilibrium (characterized by Maxwellian distribution function), and they are all small quantities for sufficiently small deviations from this state. We shall hereafter use the denotation "forces" for the quantities (3.25).

We must be able to express mathematically that the deviation from equilibrium may be said to be the cause of transport phenomena, by regarding all transport vectors or "fluxes" as functions of the "forces". A connection exists between the components of the "fluxes" and "forces". The reason for this is obviously that the deviation in the distribution function from the equilibrium distribution is a function of the forces.

We may circumvent the difficulties mentioned in the preceding section and obtain a complete set of macroscopic equations by limiting ourselves to states that are sufficiently close to equilibrium, so that we may assume the validity of a linear theory. We require that the variation in all macroscopic quantities over distances of the order of magnitude of the correlation length  $D$  be infinitesimal [8]. The distribution functions of the first or higher orders will then depend linearly on the forces (3.25).

If we write for  $f_\alpha$ ,

$$f_\alpha = f_\alpha^{(0)} + f_\alpha^{(1)}, \quad f_\alpha^{(1)} = f_\alpha^{(0)} \varphi_\alpha^{(1)}, \quad (3.27)$$

where  $f_\alpha^{(0)}$  is the equilibrium distribution (2.73), we must have

$$\varphi_\alpha^{(1)} = A_\alpha \cdot \frac{\partial \ln \mathfrak{J}}{\partial \mathbf{r}} + B_\alpha : \mathbf{e} + \sum_\beta D_{\alpha\beta} \cdot \frac{\partial \mu_\beta}{\partial \mathbf{r}}. \quad (3.28)$$

We require that  $f_\alpha^{(1)}$  must not contribute to the density, temperature and mean velocity, so that the macroscopic parameters  $n_\alpha$ ,  $\mathfrak{J}_\alpha$  and  $\mathbf{c}_{\alpha 0}$  contained in  $f_\alpha^{(0)}$  are the real density, temperature and velocity.

The vectors  $\mathbf{A}$  and  $\mathbf{D}$  and the tensor  $\mathbf{B}$  are functions of the velocity  $\mathbf{C}_\alpha$  and the magnetic field  $\mathbf{B}$ . They can be determined by substitution of (3.27) in Boltzmann's equation as described by Chapman and Cowling [4], when their form is known. We shall find the latter in Section 21.

In a similar way we must expect that the next approximation to  $f_\alpha$ , i.e.  $f_\alpha^{(2)}$ , will depend linearly on terms that are quadratic in the forces and their gradients.

It follows immediately from (3.28) that the following "phenomenological relations" must be valid,

$$\begin{aligned} (a) \quad q_\alpha \bar{\mathbf{C}}_\alpha &= - \lambda'_\alpha \cdot \frac{\partial \ln \mathfrak{J}}{\partial \mathbf{r}} - \sum_\beta \lambda_{\alpha\beta} \cdot \frac{\partial \mu_\beta}{\partial \mathbf{r}}, \\ (b) \quad \overset{\circ}{\mathbf{P}}_\alpha &= - 2 \mu_\alpha : \mathbf{e}, \\ (c) \quad \mathbf{q}_\alpha &= - \kappa_\alpha \cdot \frac{\partial \ln \mathfrak{J}}{\partial \mathbf{r}} - \sum_\beta \kappa'_{\alpha\beta} \cdot \frac{\partial \mu_\beta}{\partial \mathbf{r}}. \end{aligned} \quad (3.29)$$

The diffusion coefficient tensors  $\lambda'_\alpha$  and  $\lambda_{\alpha\beta}$  are both of the second order, and consequently have  $3^2 = 9$  components. The same is the case for the heat conduction coefficient tensors  $\kappa_\alpha$  and  $\kappa'_{\alpha\beta}$ . The viscosity coefficient tensor  $\mu_\alpha$  is of the fourth order, and consequently has  $3^4 = 81$  components.

The transport vectors  $q_\alpha \bar{\mathbf{C}}_\alpha$  and  $\mathbf{q}_\alpha$  of course only depend on the vectors  $\frac{\partial \ln \mathfrak{J}}{\partial \mathbf{r}}$  and  $\frac{\partial \mu_\beta}{\partial \mathbf{r}}$ , while the tensor  $\overset{\circ}{\mathbf{P}}$  can only depend on the tensor  $\mathbf{e}$ . The reason for this is that the "cause" and "effect" must have the same symmetrical properties (Curie's theorem).

From equation (3.29) and the relation  $\mathbf{j}_\alpha^* = e_\alpha n_\alpha \bar{\mathbf{C}}_\alpha$  it follows moreover that

$$\mathbf{j}_\alpha^* = - \frac{e_\alpha}{m_\alpha} \lambda'_\alpha \cdot \frac{\partial \ln \mathfrak{J}}{\partial \mathbf{r}} - \sum_\beta \frac{e_\alpha}{m_\alpha} \lambda_{\alpha\beta} \cdot \frac{\partial \mu_\beta}{\partial \mathbf{r}}. \quad (3.30)$$

The relations (3.29) give us  $12 \times$  new scalar equations for the macroscopic quantities (3.23) in addition to the ones we already have, and this is sufficient to complete the set of equations. (The number of sufficient equations was  $12 \times - 6$ ).

By summing (3.29) over all  $\alpha$  we get the relations

$$\begin{aligned} (a) \quad \sum_\alpha \lambda'_\alpha &= 0, \quad \sum_\alpha \lambda_{\alpha\beta} = 0, \\ (b) \quad \overset{\circ}{\mathbf{P}} &= - 2 \mu : \mathbf{e}, \\ (c) \quad \mathbf{q} &= - \kappa \cdot \frac{\partial \ln \mathfrak{J}}{\partial \mathbf{r}} - \sum_\beta \kappa'_\beta \cdot \frac{\partial \mu_\beta}{\partial \mathbf{r}}, \end{aligned} \quad (3.31)$$

where now

$$\mu = \sum_\alpha \mu_\alpha, \quad \kappa = \sum_\alpha \kappa_\alpha \quad \text{and} \quad \kappa'_\beta = \sum_\alpha \kappa'_{\alpha\beta} \quad (3.32)$$

are the new coefficient tensors.

In the same manner we derive from (3.30),  $(j^* = \sum j_\alpha^*)$ ,

$$j^* = -\sigma' \cdot \frac{\partial \ln \mathfrak{S}}{\partial r} - \sum_\beta \sigma_\beta \cdot \frac{\partial \mu_\beta}{\partial r}, \quad (3.33)$$

where the conductivity tensors  $\sigma'$  and  $\sigma_\beta$  are defined by

$$\sigma' = \sum_\alpha \frac{e_\alpha}{m_\alpha} \lambda'_\alpha, \quad \sigma_\beta = \sum_\alpha \frac{e_\alpha}{m_\alpha} \lambda_{\alpha\beta}. \quad (3.34)$$

Equation (3.33) is the generalized Ohm's law.

In the special case that the gas does not rotate ( $\frac{\partial}{\partial r} c_0 = 0$ ), and we only have electric and magnetic forces, equation (3.33) becomes identical to the generalized law already proposed by Green [8], apart from the conductivity in the latter law being a scalar.

The condition is that we assume the value (2.102) for the chemical potential, meaning that the gas is assumed to be ideal. This corresponds to the assumption made in Section 8 that the kinetic particle energy is much larger than the interaction energy  $nD^3 \gg 1$ . This assumption is highly justified in the regions of temperature and density pertinent to plasma physics. It corresponds to neglecting the correction term  $\Delta F_\alpha$  (Section 9) which is identical to the so-called virial term. This is only noticeable for real gases.

There is, however, a slight difference between our Ohm's law (3.33) and Green's law. Instead of the magnetic force  $c_0 \times B$  contained in  $\frac{\partial \mu_\alpha}{\partial r}$  (3.26), Green assumes the force  $c_{\alpha 0} \times B$ . He asserts that the Hall flow is proportional to the latter quantity, not with the former. But when assuming with Green that  $B = 0$  in the equilibrium state, the difference between the quantity  $c_0 \times B$  and  $c_{\alpha 0} \times B$  will be a second-order quantity because of the equilibrium condition  $c_{\alpha 0} = c_0$  (2.91). This quantity must be neglected in a first-order theory.

As regards Green's criticism of Spitzer's assumption (3.22), we note that the equation which Green identifies with Spitzer's equation (3.21) is valid for real gases, while Spitzer implicitly appears to have assumed that the gas is ideal, in that his point of departure is Boltzmann's equation (without correcting virial term). When comparing the two equations it is therefore necessary to confine oneself to ideal gases, especially because Green's argumentation against the assumption (3.22) is based on Chapman and Cowling's results, which are only valid for ideal gases.

For an ideal gas, where the collision term disappears in the equilibrium state, and thus also the collision contribution (3.22), it is evidently correct to develop this as a linear combination of the "forces" (3.25) when the state is sufficiently close to equilibrium. This is of course also the case for  $j^*$  (equation (3.33)), and the collision term (3.22) may consequently in general be written as a linear combination of  $j^*$  and terms involving the gradients of temperature and chemical potential. Only in the special case that these terms disappear can Spitzer's assumption (3.22) be correct, and only provided that the conductivity is a tensor.

A possible criticism must therefore also be directed against the fact that Spitzer assumes that the conductivity is a scalar. It is another matter whether there is really conformance between the actual values of the components of this tensor and the components of the real conductivity tensor in (3.33). This cannot be established before the coefficient tensors in the phenomenological relations have been evaluated by direct solution of Boltzmann's equation.

If equation (3.21) is really the generalized Ohm's law in the first approximation, and the assumption (3.22) is correct, we must, if we substitute (3.22) in (3.21), to a first approximation get an equation which is equivalent with (3.33). The result course depends on the equilibrium conditions assumed, as they determine which "forces" we are to choose.

With the assumption of his special equilibrium conditions (and wrong Hall current), Green believes to be able to establish that for a binary gas equation (3.21) cannot be identical with Ohm's law (3.33) except in the special case that the temperatures gradient  $\frac{d \ln T}{dr}$  is zero.

The case is by no means clarified, however, and a closer investigation is necessary.

## 20. SYMMETRY PROPERTIES OF THE MEDIUM

When we are to determine the form of the coefficient tensors  $A$ ,  $B$ ,  $D$ ;  $\kappa$ ,  $\lambda$ ,  $\mu$ , in the preceding section, we must take certain assumptions about the symmetry properties of the gas.

Position-dependent force fields will have no influence on the symmetry properties, and will only be able to make the medium inhomogeneous. This is the case for all electric fields, gravitational fields, etc. As concerns the only velocity-dependent force entering into our treatment, the Lorentz

force  $\frac{1}{c} \frac{e_a}{m_a} (c_a \times B)$ , the circumstances are different. The magnetic field  $B$  stresses a direction in the gas, and all molecules describe helical trajectories with this direction as an axis. The magnetic field thus introduces a systematic molecular anisotropy, which was not present in the absence of the field. As long as the gyration radius is sufficiently small, we must therefore assume that the ionized gas has the same symmetry properties as an anisotropic medium with rotational symmetry about an axis. When the magnetic field decreases the medium will become gradually isotropic.

We shall investigate the consequences of this assumption for the form of the coefficient tensor in the phenomenological relations in the preceding section. During this investigation we shall need some results that will be deduced from the theory of Cartesian tensors. (Those not interested in the details of the derivation may pass on at once to Section 22, just accepting the validity of the results of Section 21).

## 21. CARTESIAN TENSORS

A Cartesian tensor  $T_{r_1 r_2 \dots r_p}$  of the  $p$ -th order is defined in a 3-dimensional Euclidean space as a set of  $3^p$  quantities (numbers, coordinate functions, etc.) that by an orthogonal transformation of coordinates,

$$x^*_i = a_{ik} x_k + b_i, \quad a_{ik} a_{jk} = \delta_{ik}, \quad |a_{ik}| = +1, \quad (3.35)$$

is transformed in accordance with the rule

$$T^*_{i_1 i_2 \dots i_p} = a_{i_1 r_1} a_{i_2 r_2} \dots a_{i_p r_p} T_{r_1 r_2 \dots r_p}. \quad (3.36)$$

Summation is everywhere performed from 1 to 3 over indices that occur twice in the same term. The old and the new coordinates are denoted by the vectors  $x_i$  and  $x^*_i$ . A vector is a tensor of the 1-st order, and a scalar is a tensor of the 0-th order. The transform of a quantity is denoted by an asterisk.

An orthogonal transformation (3.35) is always composed of a pure translation ( $b_i = \text{Const.}$ ) and a pure rotation ( $a_{ik} x_k$ ,  $a_{ik} = \text{Const.}$ ) of the coordinate system. Rotation through an angle  $\psi$  about an axis with direction vector  $l_i$  can, according to Spain [20], be represented by the transformation matrix,

$$a_{ik} = \cos \psi \delta_{ik} + (1 - \cos \psi) l_i l_k + \sin \psi \epsilon_{ijk} l_j. \quad (3.37)$$

Here  $\epsilon_{123} = \epsilon_{312} = \epsilon_{231} = +1$ ,  $\epsilon_{321} = \epsilon_{213} = \epsilon_{132} = -1$ , and all the other  $\epsilon_{ijk} = 0$ . It can be shown that  $\delta_{ik}$  and  $\epsilon_{ijk}$  are tensors of the second and third order. If the angle of rotation  $\psi$  is infinitesimal,  $\psi = \delta\psi$ , the relation (3.37) turns into

$$a_{ik} \approx \delta_{ik} + \delta\psi \epsilon_{ijk} l_j = \delta_{ik} + S_{ik}. \quad (3.38)$$

As the inner product of the two tensors is a new tensor, then  $a_{ik}$  and  $S_{ik}$  must also be tensors, according to (3.37) and (3.38).

### 21.1 TRANSFORMATION OF LINEAR TENSOR RELATIONS

Suppose that a linear, homogeneous relation exists between the Cartesian tensor  $T_{r_1 \dots r_p}$  and another tensor  $U_{s_1 \dots s_q}$  (of the order  $q$ ),

$$T_{r_1 \dots r_p} = \kappa_{r_1 \dots r_p, s_1 \dots s_q} U_{s_1 \dots s_q}, \quad (3.39)$$

where  $T$ ,  $\kappa$  and  $U$  are functions of the coordinates  $x_i$  and the time  $t$ .

According to the quotient theorem for tensors, the  $3^{p+q}$  coefficients are components of a tensor of the order  $p+q$ . (The quotient theorem states that a set of  $3^r$  quantities are components of a tensor of the order  $r$  if the inner product of these quantities with a tensor with arbitrary components is also a tensor.) The transformation rule for the coefficient tensor is therefore



$$\kappa_{i_1 \dots i_p, j_1 \dots j_q}^* = a_{i_1 r_1} \dots a_{i_p r_p} a_{j_1 s_1} \dots a_{j_q s_q} \kappa_{r_1 \dots r_p, s_1 \dots s_q} \quad (3.40)$$

The dependence (3.39) must therefore also exist between the transformed quantities. The relation (3.39) is *invariant* with respect to coordinate transformations.

For certain transformations  $a_{ik}$ , dependent on the symmetry properties of the medium, the tensor  $\kappa_{r_1 \dots s_q}$  will be transformed into itself. If the medium, for instance, is isotropic, this will be the case for all rotations of the coordinate system; if the medium is rotationally symmetrical, for all rotations about the axis of symmetry, etc. For a homogeneous medium all coefficients  $\kappa_{r_1 \dots s_q}$  will be constant (invariance with respect to a pure translation of the coordinate system).

If we know the symmetry properties of the medium, we thus know the transformation tensors  $a_{ik}$  for which the relation

$$\kappa_{i_1 \dots i_p, j_1 \dots j_q}^* = \kappa_{i_1 \dots i_p, j_1 \dots j_q} \quad (3.41)$$

is satisfied. Together, expressions (3.40) and (3.41) then give a certain number, namely  $3^{p+q} \cdot S$ , of equations to determine the quantities  $\kappa_{r_1 \dots s_q}$ . The quantity  $S$  is the number of transformations for which (3.41) is satisfied. Only a certain number of these equations will be independent of each other, so that we cannot expect to be able to determine all the  $3^{p+q}$  coefficients completely. What we can determine by this procedure is the *form* of the coefficient tensor which corresponds to the symmetry properties of the medium.

We shall now carry out this line of reasoning in detail for the tensor relations

$$T_i = \kappa_{ir} U_r, \quad T_{ij} = \kappa_{ijrs} U_{rs} \quad (3.42)$$

under the assumption of a rotationally symmetrical medium. The quantities  $T_{ij}$  and  $U_{rs}$  are both assumed to be symmetrical.

For simplicity we place the  $x_3$ -axis of our coordinate system along the axis of symmetry. The requirement of rotational symmetry then means that the relation (3.41) must be satisfied for arbitrary rotations of the coordinate system about the  $x_3$ -axis. As this axis has the direction vector  $l_i = \delta_{i3}$ , the transformation tensor must, according to (3.37), in this case have the form

$$a_{ik} = \cos \phi \delta_{ik} + (1 - \cos \phi) \delta_{i3} \delta_{k3} + \sin \phi \epsilon_{i3k} \quad (3.43)$$

or, on matrix form,

$$[a_{ik}] = \begin{bmatrix} \cos \psi & -\sin \psi & 0 \\ \sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{bmatrix} . \quad (3.44)$$

The requirement of invariance (3.41) for  $x_{i_1 \dots j_q}$  is satisfied for arbitrary rotations  $\psi$  about the  $x_3$ -axis if it is satisfied for the three rotations  $\psi = \pi$ ,  $\psi = \pi/2$  and  $\psi = \delta\psi$  with the transformation matrices,

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} , \quad \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} , \quad \begin{bmatrix} 1 & -\delta\psi & 0 \\ \delta\psi & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} . \quad (3.45)$$

## 21.2 THE RELATION $T_i = x_{ir} U_r$

The coefficient tensor  $x_{ik}$  has the matrix

$$[x_{ik}] = \begin{bmatrix} x_{11} & x_{12} & x_{13} \\ x_{21} & x_{22} & x_{23} \\ x_{31} & x_{32} & x_{33} \end{bmatrix} . \quad (3.46)$$

In this case the invariance requirement (3.41) gives

$$x^*_{ij} = a_{ir} a_{js} x_{rs} = x_{ij} \quad \text{or} \quad (a_{ir} a_{js} - \delta_{ir} \delta_{js}) x_{rs} = 0 . \quad (3.47)$$

In this equation we successively substitute the three sets (3.45) for  $(a_{ik})$  and find the corresponding conditions for the components  $x_{rs}$ .

The requirement of invariance with respect to the rotation  $\psi = \pi$  gives the conditions  $x_{13} = x_{31} = x_{23} = x_{32} = 0$ , so that  $[x_{ik}]$  reduces to

$$[x_{ik}] = \begin{bmatrix} x_{11} & x_{12} & 0 \\ x_{21} & x_{22} & 0 \\ 0 & 0 & x_{33} \end{bmatrix} . \quad (3.48)$$

The requirements of invariance with respect to the rotation  $\psi = \pi/2$  further gives the new conditions  $x_{21} = -x_{12}$ ,  $x_{22} = x_{11}$ , and  $[x_{ik}]$  is further reduced to

$$[\kappa_{ik}] = \begin{bmatrix} \kappa_{11} & \kappa_{12} & 0 \\ -\kappa_{12} & \kappa_{11} & 0 \\ 0 & 0 & \kappa_{33} \end{bmatrix} \quad (3.49)$$

The requirement of invariance with respect to the rotation  $\psi = \delta\psi$  means that equation (3.47) is satisfied with  $a_{ik} = \delta_{ik} + S_{ik}$ ,  $S_{ik} = \delta\psi \epsilon_{ik}$ .

We have, in other words, the relation

$$(\delta_{ir} S_{js} + \delta_{js} S_{ir}) \kappa_{rs} = 0 \quad (3.50)$$

when quadratic terms in  $S_{ik}$  are neglected. These equations, however, give no new conditions, and (3.49) thus is the most general rotationally symmetric tensor of the second order.

If we so wish, we can write the relation  $T_i = \kappa_{ir} U_r$  in the familiar vector-dyadic form as  $T = \mu \cdot U$ ,  $\mu = e_i \kappa_{ik} e_k$  where  $e_i$  denotes the unit vectors in the three directions of the axes. If we use (3.49), the expression for  $T$  can be transformed to

$$T = \kappa_{11} U_{\perp} + \kappa_{12} (U \times e_3) + \kappa_{33} U_{\parallel} = \mu \cdot U, \quad (3.51)$$

where  $U_{\perp} = U_1 e_1 + U_2 e_2$  and  $U_{\parallel} = U_3 e_3$  are the components of the vector  $U$  normal to and parallel with the axis of symmetry ( $e_3$ ).

Finally we shall only note that the most general *isotropic* tensor of the second order has the form

$$\kappa_{ik} = \kappa \delta_{ik}, \quad [\kappa_{ik}] = \begin{bmatrix} \kappa & 0 & 0 \\ 0 & \kappa & 0 \\ 0 & 0 & \kappa \end{bmatrix}. \quad (3.52)$$

This can be easily verified by requiring invariance even for arbitrary rotations about the  $x_1$ - and  $x_2$ -axes.

### 21.3 THE RELATION $T_{ij} = \kappa_{ijrs} U_{rs}$

In this case the coefficient tensor has  $3^4 = 81$  components, which may be arranged on matrix form according to the following convention,

$$\begin{bmatrix}
 \kappa_{1111} & \kappa_{1122} & \kappa_{1133} & \kappa_{1123} & \kappa_{1131} & \kappa_{1112} & \kappa_{1132} & \kappa_{1113} & \kappa_{1121} \\
 \kappa_{2211} & \kappa_{2222} & \kappa_{2233} & \kappa_{2223} & \kappa_{2231} & \kappa_{2212} & \kappa_{2232} & \kappa_{2213} & \kappa_{2221} \\
 \kappa_{3311} & \kappa_{3322} & \kappa_{3333} & \kappa_{3323} & \kappa_{3331} & \kappa_{3312} & \kappa_{3332} & \kappa_{3313} & \kappa_{3321} \\
 \kappa_{2311} & \kappa_{2322} & \kappa_{2333} & \kappa_{2323} & \kappa_{2331} & \kappa_{2312} & \kappa_{2332} & \kappa_{2313} & \kappa_{2321} \\
 \kappa_{3111} & \kappa_{3122} & \kappa_{3133} & \kappa_{3123} & \kappa_{3131} & \kappa_{3112} & \kappa_{3132} & \kappa_{3113} & \kappa_{3121} \\
 \kappa_{1211} & \kappa_{1222} & \kappa_{1233} & \kappa_{1223} & \kappa_{1231} & \kappa_{1212} & \kappa_{1232} & \kappa_{1213} & \kappa_{1221} \\
 \kappa_{3211} & \kappa_{3222} & \kappa_{3233} & \kappa_{3223} & \kappa_{3231} & \kappa_{3212} & \kappa_{3232} & \kappa_{3213} & \kappa_{3221} \\
 \kappa_{1311} & \kappa_{1322} & \kappa_{1333} & \kappa_{1323} & \kappa_{1331} & \kappa_{1312} & \kappa_{1332} & \kappa_{1313} & \kappa_{1321} \\
 \kappa_{2111} & \kappa_{2122} & \kappa_{2133} & \kappa_{2123} & \kappa_{2131} & \kappa_{2112} & \kappa_{2132} & \kappa_{2113} & \kappa_{2121}
 \end{bmatrix}
 \quad (3.53)$$

If we now write  $T_{ij}$  and  $U_{ij}$  as column matrices  $[T_{ij}]$  and  $[U_{ij}]$  where the components are arranged above each other according to the following convention,

$$(T_{11} \ T_{22} \ T_{33} \ T_{23} \ T_{31} \ T_{12} \ T_{32} \ T_{13} \ T_{21}) , \quad (3.54)$$

and correspondingly for  $U_{ij}$ , the relation  $T_{ij} = \kappa_{ijrs} U_{rs}$  can be written on matrix form as

$$[T_{ij}] = [\kappa_{ijrs}] \cdot [U_{rs}] . \quad (3.55)$$

Because of the symmetry properties

$$T_{ij} = T_{ji} , \quad U_{ij} = U_{ji} , \quad (3.56)$$

only 36 of the 81 coefficients  $\kappa_{ijkl}$  are really independent. It follows from (3.56) that

$$\kappa_{ijrs} U_{rs} = \kappa_{jirs} U_{rs} = \kappa_{ijsr} U_{rs} = \kappa_{jisr} U_{rs} , \quad (3.57)$$

and as the components  $U_{rs}$  may be arbitrarily chosen, we must have that

$$\kappa_{ijrs} = \kappa_{ijsr} = \kappa_{jirs} = \kappa_{jisr} . \quad (3.58)$$

Thus  $\kappa_{ijrs}$  is symmetrical with respect to the indices  $i$  and  $j$ , and the indices  $r$  and  $s$ .

The independent coefficients are the  $6 \times 6 = 36$  in the upper left-hand corner of (3.53). The coefficients  $\kappa_{3231}$ ,  $\kappa_{2313}$ ,  $\kappa_{3213}$  are, for instance, all equal to  $\kappa_{2331}$ . We note that if  $U_{rs}$  is anti-symmetrical, then also  $\kappa_{ijrs}$  is anti-symmetrical in the indices  $r$  and  $s$ ,

$$\kappa_{ijrs} = \kappa_{jirs} = -\kappa_{ijsr} = -\kappa_{jisr} . \quad (3.59)$$

Instead of writing the whole matrix (3.53) we will henceforth only write down the 36 independent elements in the upper left-hand corner.

The invariance requirement now gives us

$$\kappa_{ijkl}^* = a_{ir} a_{js} a_{kt} a_{lu} \kappa_{rstu} = \kappa_{ijkl} ,$$

or

$$(a_{ir} a_{js} a_{kt} a_{lu} - \delta_{ir} \delta_{js} \delta_{kt} \delta_{lu}) \kappa_{rstu} = 0 . \quad (3.60)$$

We again substitute successively the three transformations matrices (3.45) representing the rotations about the  $x_3$ -axis, and obtain corresponding conditions for the coefficients  $\kappa_{ijkl}$ .

The requirement of invariance for the rotation  $\phi = \pi$  gives the condition

$$\kappa_{ijkl} = 0 \quad \text{when index 3 occurs an uneven number of times.} \quad (3.61)$$

This means that the  $6 \times 6$  - matrix for the independent quantities  $\kappa_{ijkl}$  get the following reduced form,

$$\begin{bmatrix} \kappa_{1111} & \kappa_{1122} & \kappa_{1133} & 0 & 0 & \kappa_{1112} \\ \kappa_{2211} & \kappa_{2222} & \kappa_{2233} & 0 & 0 & \kappa_{2212} \\ \kappa_{3311} & \kappa_{3322} & \kappa_{3333} & 0 & 0 & \kappa_{3312} \\ 0 & 0 & 0 & \kappa_{2323} & \kappa_{2331} & 0 \\ 0 & 0 & 0 & \kappa_{3123} & \kappa_{3131} & 0 \\ \kappa_{1211} & \kappa_{1222} & \kappa_{1233} & 0 & 0 & \kappa_{1212} \end{bmatrix} . \quad (3.62)$$

The number of independent coefficients is thus reduced from 36 to 20.

The requirement of invariance with respect to the rotation  $\phi = \pi/2$  further gives

$$\begin{aligned} \kappa_{1211} &= -\kappa_{2122}, & \kappa_{1233} &= 0, & \kappa_{1112} &= -\kappa_{2221} \\ \kappa_{3312} &= 0, & \kappa_{2323} &= \kappa_{1313}, & \kappa_{3123} &= -\kappa_{3213} \\ \kappa_{1111} &= \kappa_{2222}, & \kappa_{1122} &= \kappa_{2211}, & \kappa_{1133} &= \kappa_{2233} \\ & & \kappa_{3311} &= \kappa_{3322} . \end{aligned} \quad (3.63)$$

The number of 20 independent coefficients further reduces to 10, and (3.62) gets the form

$$\begin{bmatrix} \kappa_{1111} & \kappa_{1122} & \kappa_{1133} & 0 & 0 & \kappa_{1112} \\ \kappa_{1122} & \kappa_{1111} & \kappa_{1133} & 0 & 0 & -\kappa_{1112} \\ \kappa_{3311} & \kappa_{3311} & \kappa_{3333} & 0 & 0 & 0 \\ 0 & 0 & 0 & \kappa_{2323} & \kappa_{2331} & 0 \\ 0 & 0 & 0 & -\kappa_{2331} & \kappa_{2323} & 0 \\ \kappa_{1211} & -\kappa_{1211} & 0 & 0 & 0 & \kappa_{1212} \end{bmatrix} \quad (3.64)$$

The invariance requirement for the rotation  $\phi = \delta\phi$  with the transformation tensor  $a_{ik} = \delta_{ik} + s_{ik}$ ,  $s_{ik} = \delta\alpha_{ik}$  gives

$$s_{ir} \kappa_{rjkl} + s_{js} \kappa_{iskl} + s_{kt} \kappa_{ijtl} + s_{lu} \kappa_{ijku} = 0, \quad (3.65)$$

which leads to the relations

$$\kappa_{1211} = -\kappa_{1112}, \quad \kappa_{1212} = \frac{1}{2}(\kappa_{1111} - \kappa_{1122}). \quad (3.66)$$

The final form of the rotational symmetric coefficient matrix thus becomes

$$\begin{bmatrix} \kappa_{1111} & \kappa_{1122} & \kappa_{1133} & 0 & 0 & \kappa_{1112} \\ \kappa_{1122} & \kappa_{1111} & \kappa_{1133} & 0 & 0 & -\kappa_{1112} \\ \kappa_{3311} & \kappa_{3311} & \kappa_{3333} & 0 & 0 & 0 \\ 0 & 0 & 0 & \kappa_{2323} & \kappa_{2331} & 0 \\ 0 & 0 & 0 & -\kappa_{2331} & \kappa_{2323} & 0 \\ -\kappa_{1112} & \kappa_{1112} & 0 & 0 & 0 & \frac{1}{2}(\kappa_{1111} - \kappa_{1122}) \end{bmatrix} \quad (3.67)$$

where only 8 of the coefficients are independent.

For the sake of comparison we shall also give the result for an *isotropic medium* (invariance with respect to rotation about all three coordinate axes):

$$\kappa_{ijkl} = \kappa_1 \delta_{ij} \delta_{kl} + \kappa_2 \delta_{ik} \delta_{jl} + \kappa_3 \delta_{il} \delta_{jk}, \quad (3.68)$$

or on matrix form,

$$\begin{bmatrix} \kappa_1 + \kappa_2 + \kappa_3 & \kappa_1 & \kappa_1 & 0 & 0 & 0 \\ \kappa_1 & \kappa_1 + \kappa_2 + \kappa_3 & \kappa_1 & 0 & 0 & 0 \\ \kappa_1 & \kappa_1 & \kappa_1 + \kappa_2 + \kappa_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & \kappa_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & \kappa_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & \kappa_2 \end{bmatrix} \quad (3.69)$$

This is the most general isotropic tensor of the fourth order, which thus has three independent coefficients.

## 22. PHENOMENOLOGICAL RELATIONS FOR ROTATIONALLY SYMMETRIC MEDIUM

In the following we shall assume without further verification that the vectors and tensors we have worked with in the preceding sections are really Cartesian tensors, i.e. they are transformed in accordance with (3.36). We further assume the symmetry properties of the medium adopted in Section 20, and that all tensors we have to do with are rotationally symmetrical (or, in the non-magnetic case, isotropic).

Let us first consider the correction (3.28) to the distribution function. We suppose that the vectors  $\mathbf{A}$  and  $\mathbf{D}$  are linear functions of the thermal velocity  $\mathbf{C}$ , and that the tensor  $\mathbf{B}$  is a linear function of the symmetric and non-divergent tensor  $\mathbf{C}^0 \mathbf{C} = \mathbf{C} \mathbf{C} - \frac{1}{3} C^2 \mathbf{I}$ , i.e. that

$$\mathbf{A} = \alpha(\mathbf{C}) \cdot \mathbf{C}, \quad \mathbf{B} = \beta(\mathbf{C}) : \mathbf{C}^0 \mathbf{C}, \quad \mathbf{D} = \gamma(\mathbf{C}) \cdot \mathbf{C}, \quad (3.70)$$

( $\alpha$ ,  $\beta$  and  $\gamma$  are isotropic tensors for an isotropic medium ( $\mathbf{B} = 0$ )). As the two second-order tensors  $\alpha$  and  $\gamma$  and the fourth-order tensor  $\beta$  are rotationally symmetrical, and the former two consequently have the form (3.49), while  $\beta$  has the form (3.67), we have, according to equation (3.51), that  $\mathbf{A}$  and  $\mathbf{D}$  are linear combinations of the vectors

$$\mathbf{C}_\perp, \quad \mathbf{C} \times \mathbf{u}^0, \quad \mathbf{C}_\parallel \quad (3.71)$$

( $\mathbf{u}^0$  is the unit vector in the direction of the magnetic field), or, which is equivalent, of the vectors

$$\mathbf{C}, \quad \mathbf{C} \times \mathbf{u}^0, \quad (\mathbf{C} \times \mathbf{u}^0) \times \mathbf{u}^0. \quad (3.72)$$

A closer investigation, the details of which we shall omit here, shows that when  $\beta$  has the form (3.67), then  $\mathbf{B}$  can be written as a linear combination of the six independent, symmetric and non-divergent tensors formed by combination of the vectors (3.71) or (3.72).

If the vectors (3.72) are denoted by  $\mathbf{u}_1$ ,  $\mathbf{u}_2$  and  $\mathbf{u}_3$ , respectively, the six tensors involved are given by the expressions

$$\frac{1}{2}(\mathbf{u}_\alpha \mathbf{u}_\beta + \mathbf{u}_\beta \mathbf{u}_\alpha), \quad \alpha, \beta = 1, 2, 3. \quad (3.73)$$

All coefficients in the relations (3.70) are in general functions of the scalar value  $C$  of  $\mathbf{C}$ .

In a similar way we assume the tensors  $\kappa$ ,  $\lambda$ ,  $\sigma$  and  $\mu$  in the phenomenological relations (3.31) and (3.33) to be rotationally symmetrical, i.e. that the three first have matrices of the form

$$\begin{bmatrix} \kappa_{11} & \kappa_{12} & 0 \\ -\kappa_{12} & \kappa_{11} & 0 \\ 0 & 0 & \kappa_{33} \end{bmatrix}, \quad (3.74)$$

while the last tensor can be represented by the matrix

$$\begin{bmatrix} \mu_{1111} & \mu_{1122} & \mu_{1133} & 0 & 0 & \mu_{1112} \\ \mu_{1122} & \mu_{1111} & \mu_{1133} & 0 & 0 & -\mu_{1112} \\ \mu_{3311} & \mu_{3311} & \mu_{3333} & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu_{2323} & \mu_{2331} & 0 \\ 0 & 0 & 0 & -\mu_{2331} & \mu_{2323} & 0 \\ -\mu_{1112} & \mu_{1112} & 0 & 0 & 0 & \frac{1}{2}(\mu_{1111} - \mu_{1121}) \end{bmatrix} \quad (3.75)$$

Digressing briefly, we note that (3.74) also is the form of the dielectric tensor  $\epsilon$  in the phenomenological relation  $\mathbf{D} = \epsilon \cdot \mathbf{E}$  which is generally assumed to be valid in the study of wave propagation in ionized gases. (See for instance [3].) This appears to support our assumption about the symmetry properties of the medium.

Between the coefficients in the phenomenological equations there must exist relations that can be derived by the use of the so-called principle of microscopic reversibility [21]. These relations are the Onsager relations.

We shall not enter further into this, especially because the conditions do not appear to be quite clarified yet, but only note that we must, among other things, have

$$\begin{aligned} \kappa_{ij}(\mathbf{B}) &= \kappa_{ji}(-\mathbf{B}), & \lambda_{ij}(\mathbf{B}) &= \lambda_{ji}(-\mathbf{B}) \\ \sigma_{ij}(\mathbf{B}) &= \sigma_{ji}(-\mathbf{B}), & \mu_{ijkl}(\mathbf{B}) &= \mu_{klij}(-\mathbf{B}). \end{aligned} \quad (3.76)$$

This means that the diagonal elements and all symmetric elements in (3.74) and (3.75) must be even functions of the magnetic field  $\mathbf{B}$ , while the anti-symmetric elements must be uneven functions of the field. These conclusions are in accord with the results that may be derived by direct solution of Boltzmann's equation (Section 25).

If  $\kappa$ ,  $\lambda$ ,  $\sigma$  and  $\mu$  had been isotropic tensors, the different flux vectors, diffusions, electric current, heat of flow and flow of momentum would have been directly proportional to the corresponding forces. This is usually the case. In our case, on the other hand, this is no longer so. Fluxes are no longer parallel to the forces. A temperature gradient



$\frac{\partial \ln \Phi}{\partial \mathbf{r}}$  and a force  $\frac{\partial \mu_\alpha}{\partial \mathbf{r}}$  will, for instance, give origin to diffusion, electric current and heat flow in the three directions

$$\left(\frac{\partial \ln \Phi}{\partial \mathbf{r}}\right)_\perp \quad \frac{\partial \ln \Phi}{\partial \mathbf{r}} \times \omega^0 \quad \left(\frac{\partial \ln \Phi}{\partial \mathbf{r}}\right)_\parallel$$

and

$$\left(\frac{\partial \mu_\alpha}{\partial \mathbf{r}}\right)_\perp \quad \frac{\partial \mu_\alpha}{\partial \mathbf{r}} \times \omega^0 \quad \left(\frac{\partial \mu_\alpha}{\partial \mathbf{r}}\right)_\parallel ,$$

or in the directions

$$\frac{\partial \ln \Phi}{\partial \mathbf{r}} \quad \frac{\partial \ln \Phi}{\partial \mathbf{r}} \times \omega^0 \quad \left(\frac{\partial \ln \Phi}{\partial \mathbf{r}} \times \omega^0\right) \times \omega^0$$

and

$$\frac{\partial \mu_\alpha}{\partial \mathbf{r}} \quad \frac{\partial \mu_\alpha}{\partial \mathbf{r}} \times \omega^0 \quad \left(\frac{\partial \mu_\alpha}{\partial \mathbf{r}} \times \omega^0\right) \times \omega^0 .$$

At the same time the usual viscosity hypothesis [22] which assumes that the stress tensor is directly proportional to the deformation tensor ( $\overset{\circ}{p} = -2\mu e$ ) breaks down. This assumption is only correct for an isotropic medium ( $B = 0$ ) and must be supplanted by the more general hypothesis  $\overset{\circ}{p} = -2\mu : e$  where  $\mu$  now has the form (2.75).

For the time being the phenomenological coefficient tensors ( $\kappa$ ,  $\lambda$ ,  $\sigma$  and  $\mu$ ) are unknown parameters in a set of macroscopic equations. In Sections 24 and 25 we shall compute these quantities directly with the aid of Boltzmann's equations.

### 23. IRREVERSIBLE PROCESSES

The macroscopic equation for the internal energy, defined as average kinetic energy per unit volume, is (3.19c),

$$\frac{dU}{dt} + U \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{c}_0 + p \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{c}_0 + \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{q} + \overset{\circ}{p} : \mathbf{e} - \sum_\alpha \mathbf{q}_\alpha C_\alpha \cdot \mathbf{F}_\alpha = 0 . \quad (3.77)$$

( $\mathbf{F}_\alpha$  now contains the magnetic force  $\mathbf{c}_0 \times \omega_\alpha$ ). This equation is in accord with the energy equation given in [8], but is derived in another and more simple manner.

The usual macroscopic thermodynamic entropy equation for quasi-static processes,

$$T \frac{dS}{dt} = \frac{dU}{dt} + p \frac{d \frac{1}{\rho}}{dt} - \sum_\alpha \frac{\mu_\alpha^0}{m_\alpha} \frac{d \frac{q_\alpha}{\rho}}{dt} , \quad (3.78)$$

does not yet, like (3.77), have a microscopic justification. In this (Gibb's) equation,  $S$ ,  $U$  and  $\frac{\mu_\alpha^0}{m_\alpha}$  denote entropy, internal energy and chemical potential per unit mass, respectively. For an ideal gas  $\mu_\alpha^0$  is now given by (2.101). We introduce instead the corresponding quantities per unit volume, and with the aid of the equation of continuity (3.18 a), equation (3.78) gets the form

$$T\left(\frac{dS}{dt} + S \frac{d}{dr} \cdot c_0\right) = \frac{dU}{dt} + U \frac{d}{dr} \cdot c_0 + p \frac{d}{dr} \cdot c_0 + \sum \frac{\mu_\alpha^0}{m_\alpha} \frac{d}{dr} \cdot q_\alpha \bar{C}_\alpha . \quad (3.79)$$

Combination of (3.78) with (3.77) gives us the following expression for the entropy change,

$$\begin{aligned} T\left(\frac{dS}{dt} + S \cdot \frac{d}{dr} \cdot c_0\right) &= - \frac{d}{dr} \cdot q - \bar{p} : \bar{e} + \sum q_\alpha \bar{C}_\alpha \cdot F_\alpha + \sum \frac{\mu_\alpha^0}{m_\alpha} \frac{d}{dr} \cdot q_\alpha \bar{C}_\alpha \\ &= - \frac{d}{dr} \cdot (q - \sum \mu_\alpha^0 n_\alpha \bar{C}_\alpha) - \bar{p} : \bar{e} - \sum q_\alpha \bar{C}_\alpha \cdot \frac{d}{dr} \left(\frac{\mu_\alpha^0}{m_\alpha} - F_\alpha\right) . \end{aligned} \quad (3.80)$$

If we introduce the entropy flow

$$q_s = q - \sum \mu_\alpha^0 n_\alpha \bar{C}_\alpha \quad (3.81)$$

and the generalized chemical potential (2.107)

$$\mu_\alpha = \mu_\alpha^0 + m_\alpha \phi_\alpha , \quad (3.82)$$

where  $\phi_\alpha$  is the total potential for all force fields (gravitational fields, electromagnetic fields, centrifugal fields, etc.), equation (3.80) can be written

$$\begin{aligned} T\left(\frac{dS}{dt} + S \frac{d}{dr} \cdot c_0\right) + T \frac{d}{dr} \cdot \left(\frac{1}{T} q_s\right) &= \\ &= - q_s \cdot \frac{d \ln T}{dr} - \bar{p} : \bar{e} - \sum n_\alpha \bar{C}_\alpha \cdot \frac{d \mu_\alpha}{dr} . \end{aligned} \quad (3.83)$$

The contribution to this equation from all forces that are proportional to the mass ( $\phi_\alpha$  independent of  $\alpha$ ) is zero because of the relation  $\sum_\alpha q_\alpha \bar{C}_\alpha = 0$ .

This holds, for instance, for gravitational forces and centrifugal forces.

If we reintroduce entropy per unit mass, (3.83) gets the form

$$q T \frac{dS}{dt} + T \frac{d}{dr} \cdot \left(\frac{1}{T} q_s\right) = - q_s \cdot \frac{d \ln T}{dr} - \bar{p} : \bar{e} - \sum n_\alpha C_\alpha \cdot \frac{d \mu_\alpha}{dr} \geq 0 . \quad (3.84)$$

In this equation of continuity the right-hand side must evidently be interpreted as the source density of the entropy. If we introduce for the "fluxes"  $q$ ,  $\bar{p}$  and  $q_\alpha \bar{C}_\alpha$  the expressions in Section 19, this source density will become a quadratic form in the "forces"  $\frac{\partial \ln T}{\partial r}$ ,  $e$  and  $\frac{\partial \mu_\alpha}{\partial r}$ . We must require that this form is a positive definit. It can then be interpreted as the irreversibly dissipated amount of heat per unit volume and time. The expressions

$$q_s = \frac{\partial \ln T}{\partial r}, \quad \bar{p} = e \quad \text{and} \quad \sum n_\alpha \bar{C}_\alpha = \frac{\partial \mu_\alpha}{\partial r} \quad (3.85)$$

give the respective thermal dissipation, viscous dissipation and dissipation because of gradients in the generalized chemical potential. The last term will contain the Joule dissipation  $j^* = E^*$  (3.23). As we have seen in Section 22 the connection between "fluxes" and "forces" is strongly modified by the presence of a magnetic field. The same will consequently be the case for the dissipation.

As we have assumed the validity of (3.78) during the derivation of (3.84), the latter equation has the character of a macroscopic postulate. The validity of this postulate must be more closely investigated by comparison of (3.84) with the equation of continuity (2.14),

$$\frac{dH_\alpha}{dt} + H_\alpha \frac{\partial}{\partial r} \cdot c_0 + \frac{\partial}{\partial r} \cdot n_\alpha \overline{C_\alpha \ln f_\alpha} = \frac{\partial_c H_\alpha}{\partial t}, \quad (3.86)$$

which is derived on a microscopic base. We multiply (3.86) by  $-kT$ , sum over all  $\alpha$  and get ( $S = -kH$ ),

$$T \left( \frac{dS}{dt} + S \frac{\partial}{\partial r} \cdot c_0 \right) - T \frac{\partial}{\partial r} \cdot \left( \frac{1}{T} \sum n_\alpha kT \overline{C_\alpha \ln f_\alpha} \right) = T \dot{\sigma}, \quad (3.87)$$

where  $\dot{\sigma} = \sum \frac{\partial_c S_\alpha}{\partial t} = \frac{\partial_c S}{\partial t}$ . For quasistatic processes it can be easily shown that the entropy flow

$$q_s = - \sum n_\alpha kT \overline{C_\alpha \ln f_\alpha} = - \sum_\alpha kT \int C_\alpha f_\alpha \ln f_\alpha d c_\alpha \quad (3.88)$$

is identical to (3.81). We have, namely,

$$\delta q_s = - \sum_\alpha kT \int C_\alpha (1 + \ln f_\alpha) \delta f_\alpha d c_\alpha. \quad (3.89)$$

If we write  $\delta f_\alpha = f_\alpha - f_\alpha^{(0)} = f_\alpha^{(0)} \varphi_\alpha$  and  $\delta q_s = q_s - q_s^{(0)}$  and take into consideration that  $q_s^{(0)} = 0$ , (3.89) becomes approximatively,

$$\begin{aligned} q_s &= - \sum_\alpha kT \int C_\alpha (1 + \ln f_\alpha^{(0)} + \varphi_\alpha) f_\alpha^{(0)} \varphi_\alpha d c_\alpha \approx \\ &\approx - \sum_\alpha kT \int C_\alpha (1 + \ln f_\alpha^{(0)}) f_\alpha^{(0)} d c_\alpha = \end{aligned}$$

$$= - \sum_{\alpha} n_{\alpha} k T \overline{C_{\alpha}} (1 + \ln f_{\alpha}^{(0)}) = q - \sum_{\alpha} \mu_{\alpha}^0 n_{\alpha} \overline{C_{\alpha}} \quad (3.90)$$

We can therefore write equation (3.87) as

$$T \left( \frac{dS}{dt} + S \frac{d}{dr} \cdot \mathbf{e}_0 \right) + T \frac{d}{dr} \cdot \left( \frac{1}{T} \mathbf{q}_s \right) = T \dot{\sigma} \quad (3.91)$$

or, if we introduce the entropy per unit mass,

$$q T \frac{dS}{dt} + T \frac{d}{dr} \cdot \left( \frac{1}{T} \mathbf{q}_s \right) = q T \dot{\sigma} \geq 0 \quad (3.92)$$

The entropy source density

$$q \dot{\sigma} = q \frac{d_c S}{dt} = -k \sum_{\alpha\beta} \int \ln f_{\alpha} \left( \frac{d_c f_{\alpha}}{dt} \right)_{\beta} d\mathbf{c}_{\alpha} \quad (3.93)$$

is, as shown in Section 12 always positive. It can be evaluated microscopically by substitution of Landau's collision term in equation (3.93) and by writing  $f_{\alpha} = f_{\alpha}^{(0)} (1 + \varphi_{\alpha})$ . The form for  $\varphi_{\alpha}$  is (3.28). The coefficients in this relation must be determined with the aid of Boltzmann's equation. It is easily seen that  $q \dot{\sigma}$  becomes a quadratic form in the "forces".

Equation (3.92) is completely identical to (3.84) if this quadratic form is the same as the right-hand side of (3.84),

$$q T \dot{\sigma} = - \mathbf{q}_s \cdot \frac{d \ln T}{dr} - \overset{0}{\mathbf{p}} : \mathbf{e} - \sum_{\alpha} n_{\alpha} \overline{C_{\alpha}} \cdot \frac{d\mu_{\alpha}}{dr} \quad (3.94)$$

The quantities  $\dot{\sigma}$ ,  $\dot{\mathbf{q}}_s$ ,  $\overset{0}{\mathbf{p}}$  and  $n_{\alpha} \overline{C_{\alpha}}$  can all be evaluated when  $\varphi_{\alpha}$  is determined. By substitution in equation (3.94) we can easily verify whether this relation is correct or not. As far as we know the validity of this relation has not been established on a microscopic basis by any authors.

## PART IV. SOLUTION OF BOLTZMANN'S EQUATION

### 24. THE METHOD OF SUCCESSIVE APPROXIMATIONS

According to whether the relaxation time  $\tau_r$  for approximation to statistical equilibrium for our system is essentially less than, equal to or greater than the characteristic times  $\tau$  for other physical effects, we must distinguish between three different cases:

- (a)  $\tau_r \ll \tau$  . Collisions are of dominant significance, the state is close to statistical equilibrium.
- (b)  $\tau_r \sim \tau$  . Collisions are of the same importance as other physical effects.
- (c)  $\tau_r \gg \tau$  . Collisions are of subordinate importance. The state is far from statistical equilibrium.

For an electron-proton plasma we can put  $\tau_r$  equal to the equalization time  $\tau_1$  for momentum and energy among the electrons (2.48). By substitution of numerical values, the conditions (a), (b) and (c) become the following,

$$\frac{T^{3/2}}{n} \begin{matrix} < \\ > \end{matrix} 60 \tau \quad \begin{matrix} a \\ b \\ c \end{matrix} \quad (4.1)$$

The case (a) is only had when the density is sufficiently large and the temperature sufficiently small. In case (c) on the other hand, the density will be very small, and the temperature large.

In case (b) the state of the system will continue near statistical equilibrium if  $\tau$  is the gyration time for the particles in a magnetic field. A magnetic field will, namely, not have any effect on a Maxwellian velocity distribution. The condition is that the thermal velocity  $C_\alpha$  is much larger than the mean velocity  $c_0$  so that we can write approximatively  $c_\alpha \approx C_\alpha$ . For isotropic velocity distribution  $f_\alpha = f_\alpha(C_\alpha)$  the magnetic force term

$(\mathbf{c}_\alpha \times \boldsymbol{\omega}_\alpha) \cdot \frac{\partial f_\alpha}{\partial \mathbf{c}_\alpha}$  in Boltzmann's equation (1.56) will vanish, and the mag-

netic field will only be of importance for the higher approximation to the distribution function.

We have previously seen that we can get a complete, solvable macroscopic set of equations when we confine ourselves to the treatment of the cases (a) and (b). To achieve this we must introduce the so-called phenomenological relations that contain the unknown parameters, the coefficient tensors. In case (c) we can generally not derive any complete macroscopic set of equations, and we are restricted to a microscopic treatment.

The alternative microscopic treatment consists in a direct solution of Boltzmann's equation. As this equation is extremely complicated in the

general case and is impossible to solve in an exact manner, we must resort to approximative methods of solution. The most usual method is that of successive approximations.

This method can be described schematically as a convenient subdivision of Boltzmann's equation into two or more (possibly an infinite number of) terms, of which the mutual ratios become the expansion parameter in a series development of the distribution function  $f_\alpha$ :

$$f_\alpha = \sum_{\alpha}^{\infty} f_\alpha^{(\alpha)}.$$

By substitution of this expression in Boltzmann's equation, the 1st, 2nd, etc. approximations to  $f_\alpha$  are determined. Which quantity to choose for the expansion parameter naturally depends on the nature of actual physical problem and the assumed conditions. This, that different states for the system require different procedures, is of course a great weakness of this method.

In case (a) and (b), when intermolecular interactions (and in case (b) the effect of the magnetic field) are the dominant physical effects, the method of solution of Chapman and Enskog may be applied. This method is described in detail by Chapman and Cowling [4]. In case (c) the procedure will depend upon the different physical conditions. Chew, Low and Goldberger [23] assume, for instance, that the dominant physical effect is due to electric and magnetic fields, and completely disregard collisions. This assumption is taken as the point of departure for a determination of the distribution function by successive approximations.

In the following we shall confine ourselves to cases (a) and (b) to make comparisons with the macroscopic theory developed in earlier sections for near-equilibrium states. We shall not describe the method of solution of Chapman and Enskog, but only cite the results it leads to in the 1st and 2nd approximation. The manner of presentation is essentially that of Chapman and Cowling. Along with these authors we shall restrict ourselves to the treatment of gases with one or two components, and for the sake of coherence include both the non-magnetic and the magnetic cases.

The method of Chapman and Enskog is based on Boltzmann's equation with the short-range collision integral (1.26). But we have shown earlier that the correct form of the collision integral for ionized gases is Landau's form (1.27). Landau's collision integral does, however, like (1.26) possess exactly the formal properties essential to the application of Chapman and Enskog's method. It can be split up in the same manner as (1.26); it is, like (1.26), zero for Maxwellian velocity distribution, and has the same summation invariants ( $1, m\mathbf{c}, \frac{1}{2}m\mathbf{c}^2$ ). We must therefore assume that we can use Landau's integral, and still use Chapman and Enskog's method of solution.

Considering, however, that a critical investigation of the above is missing, we shall use the familiar integral (1.26). If our assumption that the two collision terms will lead to formally identical results is correct, then the choice of collision integral is unimportant as long as we are only interested in general formulas, and not in numerical results.

For the sake of clarity we write down Boltzmann's equation with the short-range collision integral (1.26),

$$\frac{df_\alpha}{dt} + \mathbf{C}_\alpha \cdot \frac{d\mathbf{f}_\alpha}{d\mathbf{r}} + (\mathbf{F}_\alpha + \mathbf{e}_0 \times \boldsymbol{\omega}_\alpha - \frac{d\mathbf{c}_0}{dt}) \cdot \frac{d\mathbf{f}_\alpha}{d\mathbf{c}_\alpha} + (\mathbf{C}_\alpha \times \boldsymbol{\omega}_\alpha) \cdot \frac{d\mathbf{f}_\alpha}{d\mathbf{C}_\alpha} =$$

$$-\frac{df_{\alpha}}{dC_{\alpha}} : \frac{d}{dr} c_0 = - \sum_{\beta} S_{\alpha\beta}(f_{\alpha}, f_{\beta}) = \frac{d}{dt} f_{\alpha} \quad (4.2)$$

where  $S_{\alpha\beta}$  is given by

$$S_{\alpha\beta}(f_{\alpha}, f_{\beta}) = - \iint (f_{\alpha}^* f_{\beta}^* - f_{\alpha} f_{\beta}) k_{\alpha\beta} dk dc_{\beta} \quad (4.3)$$

In the case (a) we thus assume that the collision term is dominant in (4.2) (and write for simplicity  $B = 0$ ), while in case (b) we assume that the collision term and the magnetic force field  $(C_{\alpha} \times \omega_{\alpha}) \cdot \frac{df_{\alpha}}{dC_{\alpha}}$  are the dominant terms.

#### 24.1 CASE (a). SIMPLE GAS

To determine the 1st approximation  $f^{(0)}$  to the distribution function  $f = \sum_0^{\infty} f^{(r)}$  we get

$$S(f^{(0)}, f^{(0)}) = 0 \quad (4.4)$$

which leads to Maxwellian velocity distribution

$$f^{(0)} = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( - \frac{mC^2}{2kT} \right) \quad (4.5)$$

The parameters  $n$ ,  $c_0$  and  $T$  can be interpreted as the respective real density, mean velocity and temperature if we require that the relations

$$\int \psi f^{(r)} dc = 0, \quad r = 1, 2, \dots \quad (4.5a)$$

be satisfied for each of the three summation variants  $\psi = (1, mC, \frac{1}{2}mC^2)$ .

To determine the 2nd approximation  $f^{(1)} = f^{(0)} \varphi^{(1)}$  we get the equation

$$\begin{aligned} \frac{d}{dt} f^{(0)} + C \cdot \frac{df^{(0)}}{dr} + \left( F - \frac{d}{dt} c_0 \right) \cdot \frac{df^{(0)}}{dC} - \frac{df^{(0)}}{dC} C : \frac{d}{dr} c_0 + \\ + S(f^{(0)}, f^{(0)} \varphi^{(1)}) + S(f^{(0)} \varphi^{(1)}, f^{(0)}) = 0 \end{aligned} \quad (4.6)$$

Here  $\frac{d}{dt} = \frac{\partial}{\partial t} + c_0 \cdot \frac{\partial}{\partial r}$ . The operator  $\frac{d}{dt}$  has a fixed form for each of the quantities  $(n, c_0, T)$  it works on [4]. Equation (4.6) is linear both in the "forces"  $\frac{d \ln T}{dr}$  and  $c_0$ , and moreover in  $\varphi^{(1)}$ . In accordance with Section 19,  $\varphi^{(1)}$  must therefore be a linear combination of the forces

$$\varphi^{(1)} = A \cdot \frac{\partial \ln T}{\partial r} + B : e . \quad (4.7)$$

To determine  $A$  and  $B$  we insert (4.7) into (4.6) and the coefficients before the forces  $\frac{\partial \ln T}{\partial r}$  and  $e$  are put equal to zero. In this way we get separate equations for  $A$  and  $B$ . According to these equations,  $A$  and  $B$  have the forms that might be expected for an isotropic medium (Section 22),

$$A = \alpha(C) C , \quad B = \beta(C) C^0 C . \quad (4.8)$$

Next, the coefficients  $\alpha$  and  $\beta$  are expressed as converging series of Sonine polynomials (generalized Laguerre polynomials),

$$\alpha(C) = \sum_r a_r S_r^{3/2}(\mathcal{C}^2), \quad \beta(C) = \sum_r b_r S_r^{3/2}(\mathcal{C}^2) . \quad (4.9)$$

Here the dimension-free quantity  $\mathcal{C} = \left(\frac{m}{2kT}\right)^{1/2} C$  is introduced to replace  $C$ .

We finally substitute these series in the equations for  $A$  and  $B$ , multiply the equations by  $S_r^{3/2}(\mathcal{C}^2)$  and  $S_r^{3/2}(\mathcal{C}^2)$  respectively, and integrate over velocity space. By using the orthogonality conditions for Sonine polynomials, we thereby get an infinite, linear set of equations for the coefficients  $a_r$  and another set for  $b_r$ . These sets can be solved approximately with the desired accuracy by breaking off the series after a given number of terms.

## 24.2 CASE (a). BINARY GAS

To determine the 1st approximation  $f_{\alpha}^{(0)}$  to  $f_{\alpha} = \sum_0^{\infty} f_{\alpha}^{(r)}$  ( $\alpha = 1, 2$ ) we get in a similar way as for a simple gas,

$$\sum_{\beta=1}^2 S_{\alpha\beta}(f_{\alpha}, f_{\beta}) = 0 , \quad \alpha = 1, 2 . \quad (4.10)$$

The solution of these two equations is again Maxwellian distribution with the same temperature and average velocity for the two gases,

$$f_{\alpha}^{(0)} = n_{\alpha} \left(\frac{m_{\alpha}}{2\pi kT}\right)^{3/2} \exp. \left(-\frac{m_{\alpha} C_{\alpha}^2}{2kT}\right) . \quad (4.11)$$

Here  $n_{\alpha}$ ,  $C_0$  and  $T$  are as before identical with the actual physical quantities, on the assumption that the higher approximations  $f_{\alpha}^{(r)}$ ,  $r \geq 1$  do not give any contribution. The equations for the next approximation  $f_{\alpha}^{(1)} = f_{\alpha}^{(0)} \varphi_{\alpha}^{(1)}$  are analogous with the corresponding equation (4.6) for a simple gas, and the solution has the form



$$\varphi_{\alpha}^{(1)} = A_{\alpha} \cdot \frac{\partial \ln T}{\partial r} + B_{\alpha} : e + D_{\alpha} \cdot d_{12} . \quad (3.12)$$

The vector  $d_{12}$  is defined by

$$d_{12} = \frac{\frac{m_1}{n}}{\partial r} - \frac{n_1 n_2 (m_2 - m_1)}{n q} \frac{\partial \ln p}{\partial r} - \frac{q_1 q_2}{p q} (F_1 - F_2) . \quad (4.13)$$

By some calculation we can show that (4.12) is completely equivalent with the expression (3.28). We can, namely, write

$$d_{12} = \frac{q_1 q_2}{p q} (d_1 - d_2) , \quad (4.14)$$

where

$$d_{\alpha} = \frac{1}{m_{\alpha}} \left[ \frac{\partial \mu_{\alpha}}{\partial r} - (\mu_{\alpha}^{\circ} - \frac{5}{2} kT) \frac{\partial \ln T}{\partial r} \right] . \quad (4.15)$$

As before  $\mu_{\alpha}^{\circ}$  and  $\mu_{\alpha}$  are the respective ordinary and generalized chemical potentials (2.101) and (2.107). The last term in equation (4.12) can therefore be transformed to

$$\sum_{\beta=1}^2 D_{\alpha\beta} \cdot d_{\beta} , \quad D_{\alpha 1} = -D_{\alpha 2} = \frac{q_1 q_2}{p q} D_{\alpha} . \quad (4.16)$$

If we include the part of this term which is explicitly dependent on  $\frac{\partial \ln T}{\partial r}$  in the first term of (4.12), the expression becomes precisely equal to equation (3.28).

In the same way as for a simple gas we further find that the form of  $A$ ,  $B$  and  $D$  is the one to be expected for an isotropic medium

$$A = \alpha(C) C , \quad D = \gamma(C) C , \quad B = \beta(C) C^{\circ} C . \quad (4.17)$$

The coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  are evaluated in the same way as previously.

### 24.3 CASE (b). SIMPLE AND BINARY GAS

The procedure is essentially the same as before, but to determine the 1st approximation we now get the equation

$$(C \times \omega) \cdot \frac{\partial f}{\partial C} + S(f^{(0)}, f^{(0)}) = 0 \quad (4.18)$$

for a simple gas, and

$$(C_{\alpha} \times \omega_{\alpha}) \cdot \frac{\partial f_{\alpha}}{\partial C_{\alpha}} + \sum_{\beta=1}^2 S_{\alpha\beta}(f_{\alpha}^{(0)}, f_{\beta}^{(0)}) = 0 \quad (4.19)$$

for a binary gas. This again leads to Maxwellian distribution in the 1st approximation. For the next approximation  $f^{(1)} = f^{(0)} \varphi^{(1)}$  we again get the expressions (4.7) for a simple gas and (4.12) for a binary gas. As opposed to the previous cases, however,  $A$ ,  $B$  and  $D$  get the forms (3.70) to be expected for a rotationally symmetric medium,

$$A = \alpha(C) \cdot C, \quad D = \gamma(C) \cdot C, \quad B = \beta(C) : C^0 C, \quad (4.20)$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are all rotationally symmetric tensors. According to Section 22 we can then write  $A$  and  $D$  as

$$A = \alpha^I(C) C + \alpha^{II}(C) C \times \omega^0 + \alpha^{III}(C) (C \times \omega^0) \times \omega^0, \quad (4.21)$$

$$D = \gamma^I(C) C + \gamma^{II}(C) C \times \omega^0 + \gamma^{III}(C) (C \times \omega^0) \times \omega^0,$$

while  $B$  is a linear combination of the six independent, divergency-free and symmetric tensors that may be found by combination of the vectors  $C$ ,  $C \times \omega^0$ ,  $(C \times \omega^0) \times \omega^0$ . These tensors are given by the expressions (3.72a). The coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  can be evaluated in the same way as previously, but it is evident that it would be very complicated to carry out the evaluations in practice. The procedure is, of course, the same if the number of components of the gas is greater than two.

Now having formally determined the 1st and 2nd approximations to the distribution functions, we shall use this in the following section to find the expressions for the transport vectors.

## 25. EVALUATION OF THE TRANSPORT VECTORS

The transport vectors or fluxes in which we are interested are, as before, diffusion, current density, transport of momentum and the heat flow, i.e. the quantities

$$q_\alpha C_\alpha, \quad j_\alpha^* = e_\alpha n_\alpha \bar{C}_\alpha, \quad \bar{P}_\alpha = n_\alpha \overline{m_\alpha C_\alpha^0 C_\alpha}, \quad q_\alpha = n_\alpha \overline{\frac{1}{2} m_\alpha C_\alpha^2 C_\alpha}. \quad (4.22)$$

If the series of approximations to  $f_\alpha$  converge sufficiently rapidly, which is the case if the temperature is sufficiently small and the density is sufficiently large (4.1), the two first terms in the series,  $f_\alpha^{(0)} + f_\alpha^{(1)}$  will give a good approximation to  $f_\alpha$ . The function  $f_\alpha^{(1)} = f^{(0)} \varphi_\alpha^{(1)}$  is given by (4.12). The contribution to (4.22) from the 1st approximation  $f_\alpha^{(0)}$  is zero, as all these quantities are zero in the state of equilibrium. The contribution from the 2nd approximation is

$$\begin{aligned}
 (a) \quad q_{\alpha} \bar{C}^{(1)} &= - \bar{\lambda}'_{\alpha} \cdot \frac{\partial \ln T}{\partial r} - \bar{\lambda}_{\alpha} \cdot d_{12} \\
 (b) \quad \frac{o}{P_{\alpha}}^{(1)} &= -2\bar{\mu}_{\alpha} : e \\
 (c) \quad q_{\alpha}^{(1)} &= - \bar{\kappa}_{\alpha} \cdot \frac{\partial \ln T}{\partial r} - \bar{\kappa}'_{\alpha} \cdot d_{12} \\
 (d) \quad j_{\alpha}^{*(1)} &= - \bar{\sigma}'_{\alpha} \cdot \frac{\partial \ln T}{\partial r} - \bar{\sigma}_{\alpha} \cdot d_{12}
 \end{aligned} \tag{4.23}$$

where the coefficients are defined by

$$\begin{aligned}
 - \bar{\lambda}'_{\alpha} &= \int m_{\alpha} C_{\alpha} A f_{\alpha}^{(0)} d\mathbf{c}_{\alpha}, & - \bar{\lambda}_{\alpha} &= \int m_{\alpha} C_{\alpha} D_{\alpha} f_{\alpha}^{(0)} d\mathbf{c}_{\alpha}, \\
 -2\bar{\mu}_{\alpha} &= \int m_{\alpha} C_{\alpha} C_{\alpha} B_{\alpha} f_{\alpha}^{(0)} d\mathbf{c}_{\alpha}, \\
 - \bar{\kappa}_{\alpha} &= \int \frac{1}{2} m_{\alpha} C_{\alpha}^2 C_{\alpha} A_{\alpha} f_{\alpha}^{(0)} d\mathbf{c}_{\alpha}, & - \bar{\kappa}'_{\alpha} &= \int \frac{1}{2} m_{\alpha} C_{\alpha}^2 C_{\alpha} D_{\alpha} f_{\alpha}^{(0)} d\mathbf{c}_{\alpha}, \\
 - \bar{\sigma}'_{\alpha} &= \int e_{\alpha} C_{\alpha} A_{\alpha} f_{\alpha}^{(0)} d\mathbf{c}_{\alpha}, & - \bar{\sigma}_{\alpha} &= \int e_{\alpha} C_{\alpha} D_{\alpha} f_{\alpha}^{(0)} d\mathbf{c}_{\alpha}.
 \end{aligned} \tag{4.24}$$

For  $A$ ,  $B$  and  $D$  we further substitute the quantities (4.20). It is then easily shown that the six second-order coefficient tensors included in the equations (4.23 a-c-d) have precisely the expected symmetry properties, i.e. they are rotationally symmetrical.

The corresponding circumstances are not so easily shown in the case of equation (4.23 b), but evaluations which will be omitted here, show that the fourth-order tensor is also rotationally symmetrical. When the magnetic field disappears,  $A$ ,  $B$  and  $D$  are given by (4.17) and all coefficients (4.24) will be isotropic tensors.

The equations (4.23) which are derived by microscopic theory therefore are completely equivalent with the corresponding phenomenological set (3.29-30). The choice of other "forces" ( $\frac{\partial \ln T}{\partial r}$ ,  $e$ ,  $d_{\alpha}$  (4.15)) is of course unimportant, as they are linear combinations of our original "forces" ( $\frac{\partial \ln T}{\partial r}$ ,  $e$ ,  $\frac{\partial \mu_{\alpha}}{\partial r}$ ). The coefficients  $\kappa$ ,  $\lambda$ ,  $\sigma$  and  $\mu$  in Section 19 are therefore given linear combinations of the coefficients (4.24) (especially  $\mu = \bar{\mu}$ ). They can therefore be evaluated when  $A$ ,  $B$  and  $D$  are determined in the manner sketched in the previous section.

In the following we denote the respective non-magnetic and magnetic cases by (a) and (b) as before.

## 25.1 CASE (a) AND (b). SIMPLE GAS

In this case  $d_{12} = 0$  and (4.23) gets the form

$$\begin{aligned} (a) \quad q \bar{C}^{(1)} &= 0 & (c) \quad j^{*(1)} &= 0 \\ (b) \quad p^{(1)} &= -2'(\mu : e & (d) \quad q^{(1)} &= -\bar{\kappa} \cdot \frac{\partial \ln T}{\partial r} \end{aligned} \quad (4.25)$$

If we substitute for  $\mathbf{A}$  and  $\mathbf{B}$  the values obtained by breaking off the series of Sonine polynomials (4.9) after the first term, we get, according to Chapman and Cowling [4] for the heat flow,

$$q^{(1)} = -(\bar{\kappa})_1 \left[ \frac{1}{1+\omega^2 \tau^2} \left( \frac{\partial \ln T}{\partial r} \right)_\perp + \frac{\omega \tau}{1+\omega^2 \tau^2} \frac{\partial \ln T}{\partial r} \times \omega^0 + \left( \frac{\partial \ln T}{\partial r} \right)_\parallel \right]. \quad (4.26)$$

Here  $(\bar{\kappa})_1$  denotes the first approximation to the heat conduction coefficient, and  $\tau$  is defined as

$$\tau = \frac{2m}{5kp} (\bar{\kappa})_1. \quad (3.27)$$

For solid, spherical molecules this is identical to the collision time for the molecules, apart from numerical factors [4]. Even when the molecules are electrically charged, as in our case, can we give a similar interpretation to  $\tau$ . The factor  $\omega \tau$  is therefore essentially the ratio between the collision time and gyration time in the magnetic field.

Equation (4.26) means that the heat flow coefficient is given by the matrix

$$(\bar{\kappa})_1 = (\bar{\kappa})_1 \begin{bmatrix} \frac{1}{1+\omega^2 \tau^2} & \frac{\omega \tau}{1+\omega^2 \tau^2} & 0 \\ \frac{-\omega \tau}{1+\omega^2 \tau^2} & \frac{1}{1+\omega^2 \tau^2} & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (4.28)$$

The form of this matrix is precisely as expected. We see, for instance, that the non-diagonal and anti-symmetric elements are linear in the magnetic field, in conformity with the Onsager relations (3.76).

We see that the factor  $\omega \tau$  is a measure of the anisotropy of the system. If we put  $\omega \tau = 0$ , then (4.28) gives the value we must have for  $(\bar{\kappa})_1$  in the non-magnetic case, i.e.  $(\bar{\kappa})_1 = (\bar{\kappa})_1 \mathbb{I}$ .

We see from (4.26) that the heat flow parallel to a magnetic field will not be influenced by the field. When  $\omega \tau$  grows from zero towards unity, the flow in the direction of  $-(\frac{\partial \ln T}{\partial r})_\perp$  will gradually decrease, while a

"Hall flow" is a set up in the direction  $-\frac{\partial \ln T}{\partial \mathbf{r}} \times \mathbf{e}^0$ . This flow is at a maximum when  $\omega\tau = 1$  and decreases like the usual transverse current when  $\omega\tau$  grows. For very strong magnetic fields ( $\omega\tau \gg 1$ ) we must expect, according to (4.26), that the heat flow across the field becomes completely subdued. The reason for this is of course that the effective mean free path across the field in this case no longer is  $\lambda = \bar{c} \cdot \tau$  but the Larmor radius  $q = \frac{\bar{c}}{\omega} = \frac{\lambda}{\omega\tau}$ . The usual free path is "curled up" around the field lines.

Chapman and Cowling further give, without proof, the first approximation to  $\mathbf{p}$  with the remark that the result is of little interest because the corresponding phenomena cannot be observed in metals (!). The result is given on a component form which is not easily read, but closer scrutiny shows that the results correspond to equation (4.25) with the coefficient tensors

$$2(\mu)_1 = 2(\mu)_1 \begin{bmatrix} \frac{1+8/9\omega^2\tau^2}{1+16/9\omega^2\tau^2} & \frac{8/9\omega^2\tau^2}{1+16/9\omega^2\tau^2} & 0 & 0 & 0 & \frac{2/3\omega\tau}{1+4/9\omega^2\tau^2} \\ \frac{8/9\omega^2\tau^2}{1+16/9\omega^2\tau^2} & \frac{1+8/9\omega^2\tau^2}{1+16/9\omega^2\tau^2} & 0 & 0 & 0 & \frac{-2/3\omega\tau}{1+4/9\omega^2\tau^2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{1+4/9\omega^2\tau^2} & \frac{-2/3\omega\tau}{1+4/9\omega^2\tau^2} & 0 \\ 0 & 0 & 0 & \frac{2/3\omega\tau}{1+4/9\omega^2\tau^2} & \frac{1}{1+4/9\omega^2\tau^2} & 0 \\ \frac{-2/3\omega\tau}{1+4/9\omega^2\tau^2} & \frac{2/3\omega\tau}{1+4/9\omega^2\tau^2} & 0 & 0 & 0 & \frac{1}{1+16/9\omega^2\tau^2} \end{bmatrix} \quad (4.29)$$

The 1st approximation to the viscosity coefficient  $(\mu)_1$  is given by

$$(\mu)_1 = \frac{2}{3} p \tau, \quad (4.30)$$

where  $\tau$  is defined by (4.27) as before.

The form of the matrix is again as expected. The non-diagonal and anti-symmetric elements are linear in the field. The Onsager relations (3.76) are thus once more satisfied. If we write  $\omega\tau = 0$  equation (4.29) gives the result obtained for  $2(\mu)_1$  in the non-magnetic case (Section 21). At the opposite extreme,  $\omega\tau \rightarrow \infty$ , all elements in (4.29), except the nine elements in the upper left-hand corner, approach zero, and the coefficient matrix once more becomes isotropic. The stress tensor now becomes

$$\begin{aligned} p_{11}^{(1)} &= p_{22}^{(1)} = -(\mu)_1 (e_{11}^0 + e_{22}^0) = (\mu)_1 e_{33}^0, \\ p_{33}^{(1)} &= -2(\mu)_1 e_{33}^0, \quad p_{ij}^{(1)} = 0, \quad (i \neq j). \end{aligned} \quad (4.31)$$

If  $e_{33}$  is zero, which is the case if the gas moves along the magnetic field with the velocity  $w_0 = w_0(r_\perp)$  the viscous forces will completely disappear.

It has been discussed whether or not the derived value of the viscosity tensor is correct. There can scarcely be any doubt that the result is correct, and it is even supported by other works. It is another matter if one can simply assume that (4.29) is valid when  $\omega\tau \gg 1$ . This appears to conflict with the assumptions for the validity of the method of solution used in Section 24, and corresponds to a situation where the term  $(C \times w) \cdot \frac{dC}{dC}$  in Boltzmann's equation is dominant, and the collision term must be regarded as a perturbation.

## 25.2 CASE (a) AND (b). BINARY GAS

According to (4.23) the relative diffusion is given by

$$\bar{C}_1 - \bar{C}_2 = - \frac{q}{q_1 q_2} \left[ \bar{\lambda}'_1 \cdot \frac{\partial \ln T}{\partial r} + \bar{\lambda}_1 \cdot d_{12} \right], \quad (4.32)$$

as the relations  $\sum_\alpha \bar{\lambda}'_\alpha = \sum_\alpha \bar{\lambda}_\alpha = 0$  must be satisfied. By constant temperature, the 1st approximation to (4.32) is, according to Chapman and Cowling,

$$\bar{C}_1^{(1)} - \bar{C}_2^{(1)} = - \frac{q}{q_1 q_2} (\bar{\lambda}_1)_1 \left[ \frac{1}{1 + \omega^2 \tau^2} (d_{12})_\perp + \frac{\omega \tau}{1 + \omega^2 \tau^2} d_{12} \times w^0 + (d_{12})_\parallel \right]. \quad (4.33)$$

Here  $(\bar{\lambda}_1)_1$  is the 1st approximation to the diffusion coefficient, and  $\omega$  and  $\tau$  are given by the expressions

$$\omega = \frac{1}{q} (q_2 \omega_1 + q_1 \omega_2), \quad \tau = \frac{1}{p} (\bar{\lambda}_1)_1.$$

Thus  $\omega$  is an average gyro frequency for the two component gases. In a similar way we can show that for solid, spherical molecules  $\tau$  is the average collision time for the two components.

We can continue to give the same interpretations to  $\tau$  when the molecules are electrically charged. As the current density  $j^*$  is proportional to (4.33) according to (3.8), we immediately find the expression

$$j^{*(1)} = - \left( \frac{e_1}{m_1} - \frac{e_2}{m_2} \right) (\bar{\lambda}_1)_1 \left[ \frac{1}{1 + \omega^2 \tau^2} (d_{12})_\perp + \frac{\omega \tau}{1 + \omega^2 \tau^2} d_{12} \times w^0 + (d_{12})_\parallel \right]. \quad (4.34)$$

This "Ohm's law" shows, together with (4.33) that both the diffusion coefficient tensor and the conductivity tensor have the expected form (4.28).

Chapman and Cowling do not give an expression for the heat flow and the viscosity tensor in the magnetic case, but we must expect that the coefficient tensors have the form (4.28-29) even in this case.

The expressions found in the non-magnetic case are in complete accord with (4.23) for an isotropic medium. The expressions (4.33) and (4.34) reduce to the corresponding expressions for the non-magnetic case when  $\omega \tau$  is put equal to zero.

## APPENDIX

The summational invariants  $\Phi$  of the Landau collision term (2.18) are characterized by having the property

$$n \frac{\partial_c \Phi}{\partial t} = \sum_{\alpha\beta} n_\alpha \left( \frac{\partial_c \bar{\Phi}_\alpha}{\partial t} \right)_\beta = \frac{1}{2} \sum_{\alpha\beta} \left[ n_\alpha \left( \frac{\partial_c \Phi_\alpha}{\partial t} \right)_\beta + n_\beta \left( \frac{\partial_c \Phi_\beta}{\partial t} \right)_\alpha \right] = 0, \quad (\text{A.1})$$

where

$$n_\alpha \left( \frac{\partial_c \bar{\Phi}_\alpha}{\partial t} \right)_\beta = \int \Phi_\alpha \left( \frac{\partial_c f_\alpha}{\partial t} \right)_\beta d\mathbf{c}.$$

They may be found in the following manner.

Using equation (2.18) we get by partial integration ( $\kappa_{\alpha\beta} = 2\pi\lambda e_\alpha^2 e_\beta^2$ ):

$$n_\alpha \left( \frac{\partial_c \bar{\Phi}_\alpha}{\partial t} \right)_\beta = \kappa_{\alpha\beta} \iint \frac{1}{m_\alpha} \frac{\partial \Phi_\alpha}{\partial \mathbf{c}} \cdot \mathbf{U} \cdot \left( \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial \mathbf{c}'} - \frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial \mathbf{c}} \right) f_\alpha f'_\beta d\mathbf{c} d\mathbf{c}', \quad (\text{A.2})$$

and analogously

$$n_\beta \left( \frac{\partial_c \bar{\Phi}_\beta}{\partial t} \right)_\alpha = \kappa_{\beta\alpha} \iint \frac{1}{m_\beta} \frac{\partial \Phi'_\beta}{\partial \mathbf{c}'} \cdot \mathbf{U} \cdot \left( \frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial \mathbf{c}} - \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial \mathbf{c}'} \right) f'_\beta f_\alpha d\mathbf{c}' d\mathbf{c}. \quad (\text{A.3})$$

Summing these two equations we get

$$\begin{aligned} n_\alpha \left( \frac{\partial_c \bar{\Phi}_\alpha}{\partial t} \right)_\beta + n_\beta \left( \frac{\partial_c \bar{\Phi}_\beta}{\partial t} \right)_\alpha = & -\kappa_{\alpha\beta} \iint \left( \frac{1}{m_\beta} \frac{\partial \Phi'_\beta}{\partial \mathbf{c}'} - \frac{1}{m_\alpha} \frac{\partial \Phi_\alpha}{\partial \mathbf{c}} \right) \cdot \mathbf{U} \cdot \\ & \cdot \left( \frac{1}{m_\beta} \frac{\partial \ln f'_\beta}{\partial \mathbf{c}'} - \frac{1}{m_\alpha} \frac{\partial \ln f_\alpha}{\partial \mathbf{c}} \right) f_\alpha f'_\beta d\mathbf{c} d\mathbf{c}'. \end{aligned} \quad (\text{A.4})$$

It is at once evident that only the three molecular properties

$$\Phi = 1 \text{ (Const.)}, \quad m\mathbf{c}, \quad \frac{1}{2}m\mathbf{c}^2 \quad (\text{A.5})$$

will make this integral and  $n \frac{\partial_c \Phi}{\partial t}$  zero. Consequently, these are the summational invariants.

(We also notice that substitution of  $\Phi = \ln f$  in (A.4) at once gives us the proof of the H-theorem.)



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